

# The crystal structures of methyl prop-2-ynoate, dimethyl fumarate and their protonated species

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Methyl prop-2-ynoate ( $C_4H_4O_2$ ) was investigated in the binary superacidic system  $HF/MF_5$  ( $M = Sb$  or  $As$ ) and dimethyl fumarate ( $C_6H_8O_4$ ) in the superacidic system  $HF/SbF_5$ , as well as  $HF/BF_3$ . The starting materials methyl prop-2-ynoate and dimethyl fumarate were crystallized, the former for the first time. The protonated species of these esters, namely, (1-methoxyprop-2-yn-1-ylidene)oxidanium hexafluoroarsenate,  $C_4H_5O_2^+ AsF_6^-$ , 1,4-dimethoxy-4-oxobut-2-en-1-ylidene]oxidanium tetrafluoroborate bis(hydrogen fluoride),  $C_6H_9O_4^+ BF_4^- \cdot 2HF$ , and hemi{[1,4-dimethoxy-4-oxidaniumylidenebut-2-en-1-ylidene]oxidanium} undecafluorodiantimonate,  $0.5C_6H_{10}O_4^{2+} Sb_2F_{11}^-$ , were characterized by single-crystal X-ray diffraction and Raman spectroscopy. The protonated species were recrystallized from anhydrous hydrogen fluoride. In the solid state of the monoprotonated species of methyl prop-2-ynoate and the diprotonated species of dimethyl fumarate, strong intramolecular  $O-H \cdots F$  hydrogen bonds build a three-dimensional network. The monoprotonated species of dimethyl fumarate builds chains by strong  $O-H \cdots O$  hydrogen bonds between the cations.

## 1. Introduction

Protonated esters have occur in two conformations, namely, *syn-anti* and *syn-syn* (Hogeveen, 1967; Olah *et al.*, 1967, 2009). The *syn-anti* conformation is more stable and is therefore consistent with the protonation of carboxylic acids (Olah *et al.*, 2009; Hollenwager *et al.*, 2024b; Hogeveen, 1968). The two conformers were observed in solution by NMR spectroscopy (Olah *et al.*, 2009). It has not yet been possible to crystallize the *syn-syn* conformer of protonated esters in the solid state; the example of prop-2-ynoic acid (propionic acid) shows that this could be achieved with a H/D exchange and solid-state effects through a larger anion (Hollenwager *et al.*, 2024b). In magic acid ( $FSO_3H/SbF_5$ ), the esters show the unimolecular cleavage of methanol by warming to 20 °C (Olah *et al.*, 2009). An exception was observed with glycine methyl ester, which is still stable in magic acid even at 93 °C (Hollenwager, *et al.*, 2024a).

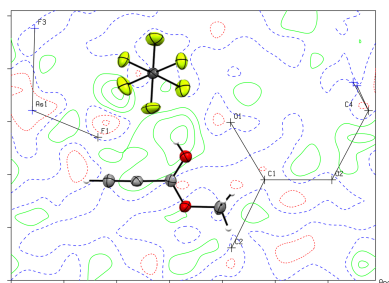
The isolation of protonated esters enables the characterization of an important intermediate that is present in solution in every acid-catalyzed esterification process. The selected esters also offer the possibility of further functionalization steps due to the double and triple bonds present. This prompted us to investigate methyl prop-2-ynoate and dimethyl fumarate in the binary superacidic media  $HF/MF_5$ .

## 2. Experimental

### 2.1. Synthesis and crystallization

#### 2.1.1. $[C_4H_5O_4][MF_6]$ ( $M = Sb$ or $As$ )

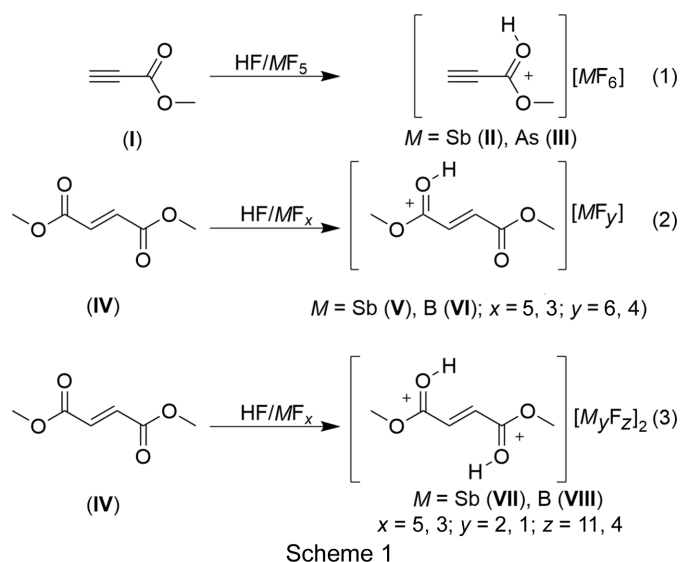
The Lewis acids ( $SbF_5$ : 433 mg, 2 mmol;  $AsF_5$ : 340 mg, 2 mmol) were each condensed into a fluorine-passivated FEP



reactor. Anhydrous hydrogen fluoride (0.5 l) was added as reactant and solvent at  $-196\text{ }^{\circ}\text{C}$ . The mixture was homogenized at room temperature. Methyl prop-2-ynoate (83.6  $\mu\text{l}$ , 84.1 mg, 1.0 mmol) was added at  $-196\text{ }^{\circ}\text{C}$  under nitrogen. The mixture was allowed to warm to room temperature. The solvent was removed overnight at  $-78\text{ }^{\circ}\text{C}$ . The protonated species **II** and **III** were obtained as white solids (Scheme 1).

### 2.1.2. $[\text{C}_6\text{H}_9\text{O}_4][\text{MF}_y]$ ( $M = \text{Sb}$ or $\text{B}$ ; $y = 6$ or $4$ )

The Lewis acids ( $\text{SbF}_5$ : 216 mg, 1 mmol;  $\text{BF}_3$ : 67 mg, 1 mmol) were each condensed into a fluorine-passivated FEP reactor. Anhydrous hydrogen fluoride (0.5 l) was added as reactant and solvent at  $-196\text{ }^{\circ}\text{C}$ . The mixture was homogenized at room temperature. Dimethyl fumarate (144 mg, 0.5 mmol) was added at  $-196\text{ }^{\circ}\text{C}$  under nitrogen. The mixture was allowed to warm to room temperature. The solvent was removed overnight at  $-78\text{ }^{\circ}\text{C}$ . The protonated species **V** and **VI** were obtained as white solids (Scheme 1). A clean Raman spectrum of monoprotonated species **VI** could not be obtained because it contains impurities of either **IV** or **VII**.

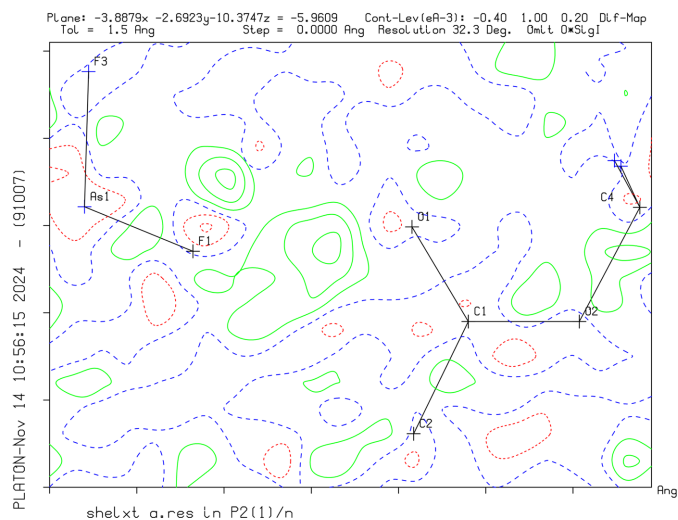


### 2.1.3. $[\text{C}_6\text{H}_{10}\text{O}_4][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{C}_6\text{H}_{10}\text{O}_4][\text{BF}_4]$

The Lewis acids ( $\text{SbF}_5$ : 216 mg, 1 mmol;  $\text{BF}_3$ : 67 mg, 1 mmol) were each condensed into a fluorine-passivated FEP reactor. Anhydrous hydrogen fluoride (0.5 l) was added as reactant and solvent at  $-196\text{ }^{\circ}\text{C}$ . The mixture was homogenized at room temperature. Dimethyl fumarate (48 mg, 0.33 mmol) was added at  $-196\text{ }^{\circ}\text{C}$  under nitrogen. The mixture was allowed to warm to room temperature. The solvent was removed overnight at  $-78\text{ }^{\circ}\text{C}$ . The protonated species **VII** and **VIII** were obtained as white solids.

## 2.2. Single-crystal X-ray diffraction and Raman spectroscopic analysis

Compounds **I**, **III**, **VI** and **VII** were characterized by single-crystal X-ray diffraction. Complete data and devices for the X-ray measurements are listed in the CIF in the supporting information. Low-temperature Raman spectroscopic analysis

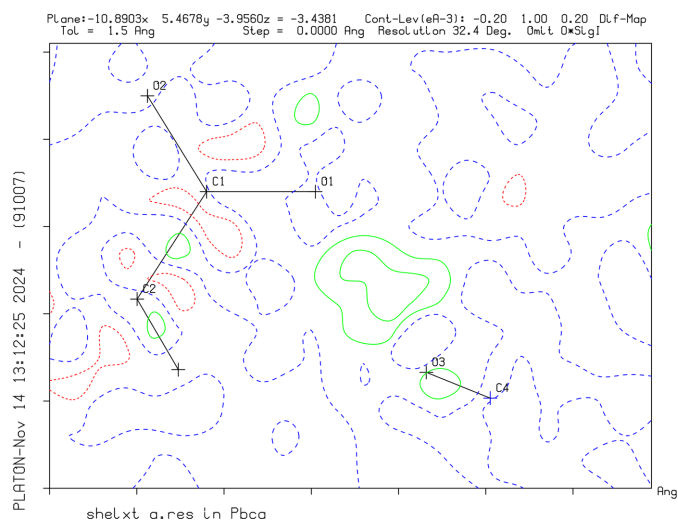


**Figure 1**  
A difference Fourier map of **III** without the H atom between O1 and F1. The green solid lines and red dotted lines show positive and negative density distribution, respectively.

was performed for **I–VIII** using a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation ( $\lambda = 1064\text{ cm}^{-1}$ ) under vacuum. For the measurements, the synthesized compound was transferred to a cooled glass cell.

## 2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The successful protonation of the target molecules was confirmed by the charge of the asymmetric unit, as well as the interatomic distances. C–O distances have become nearly equal after protonation, as the charge can formally be localized on the C atom resulting in the loss of double-bond character. The positions of the H atoms were identified by Q-peaks on the difference Fourier map and



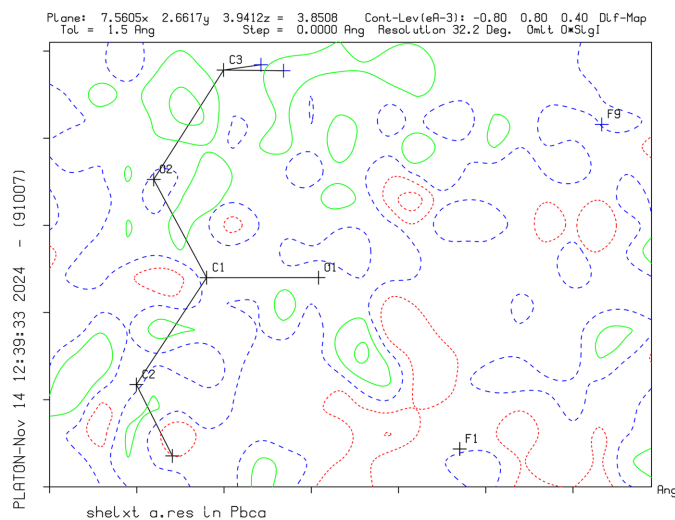
**Figure 2**  
A difference Fourier map of **VI** without the H atom between O1 and F1. The green solid lines and red dotted lines show positive and negative density distribution, respectively.

**Table 1**  
Experimental details.

Experiments were carried out with Mo  $K\alpha$  radiation using a Rigaku Xcalibur Sapphire3 diffractometer. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2020).

	I	III	IV
<b>Crystal data</b>			
Chemical formula	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>5</sub> O <sub>2</sub> <sup>+</sup> ·AsF <sub>6</sub> <sup>-</sup>	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>
$M_r$	84.07	274.00	144.12
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
temperature (K)	111	111	112
$a, b, c$ (Å)	3.8409 (5), 15.593 (2), 7.6149 (10)	6.9609 (5), 8.9319 (7), 13.7189 (9)	3.8726 (11), 5.6546 (10), 8.3778 (18)
$\alpha, \beta, \gamma$ (°)	90, 99.910 (12), 90	90, 91.664 (7), 90	100.642 (16), 100.42 (2), 105.73 (2)
$V$ (Å <sup>3</sup> )	449.27 (10)	852.60 (11)	168.30 (7)
$Z$	4	4	1
$\mu$ (mm <sup>-1</sup> )	0.10	4.06	0.12
Crystal size (mm)	1.00 × 0.56 × 0.31	0.90 × 0.21 × 0.15	0.52 × 0.46 × 0.35
<b>Data collection</b>			
$T_{\min}, T_{\max}$	0.457, 1.000	0.582, 1.000	0.579, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	3885, 1060, 891	4205, 2303, 1900	1403, 825, 703
$R_{\text{int}}$	0.023	0.029	0.015
$\theta_{\text{max}}$ (°)	27.9	29.1	28.3
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.658	0.685	0.667
<b>Refinement</b>			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.099, 1.05	0.039, 0.099, 1.05	0.048, 0.144, 1.04
No. of reflections	1060	2303	825
No. of parameters	71	123	51
No. of restraints	0	0	0
H-atom treatment	All H-atom parameters refined	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.18, -0.15	0.87, -0.92	0.52, -0.24
<hr/>			
	<b>VI</b>	<b>VII</b>	
<b>Crystal data</b>			
Chemical formula	C <sub>6</sub> H <sub>9</sub> O <sub>4</sub> <sup>+</sup> ·BF <sub>4</sub> <sup>-</sup> ·2HF	0.5C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> <sup>2+</sup> ·Sb <sub>2</sub> F <sub>11</sub> <sup>-</sup>	
$M_r$	271.96	525.57	
Crystal system, space group	Orthorhombic, $Pbca$	Orthorhombic, $Pbca$	
temperature (K)	101	101	
$a, b, c$ (Å)	12.8759 (5), 11.8899 (4), 14.6252 (7)	7.8461 (6), 15.1531 (11), 19.5536 (17)	
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 90, 90	
$V$ (Å <sup>3</sup> )	2239.02 (16)	2324.8 (3)	
$Z$	8	8	
$\mu$ (mm <sup>-1</sup> )	0.19	4.79	
Crystal size (mm)	0.28 × 0.18 × 0.11	0.25 × 0.11 × 0.05	
<b>Data collection</b>			
$T_{\min}, T_{\max}$	0.885, 1.000	0.807, 1.000	
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	7514, 1717, 1478	13316, 3784, 2878	
$R_{\text{int}}$	0.026	0.053	
$\theta_{\text{max}}$ (°)	23.8	32.2	
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.568	0.750	
<b>Refinement</b>			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.100, 1.05	0.036, 0.071, 1.04	
No. of reflections	1717	3784	
No. of parameters	176	169	
No. of restraints	1	0	
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.77, -0.35	1.09, -1.01	

computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).



**Figure 3**  
A difference Fourier map of **VII** without the H atom between O1 and F1. The green solid lines and red dotted lines show positive and negative density distribution, respectively.

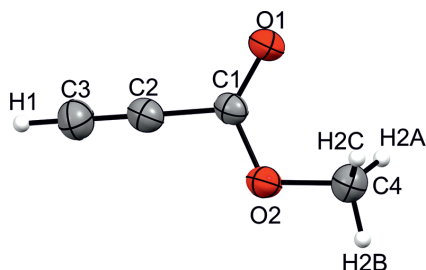
by evaluation of the contacts (Figs. 1–3). Methyl, methylene and acetylenic H atoms were refined under restrictions and the proton positions were modulated.

### 3. Results and discussion

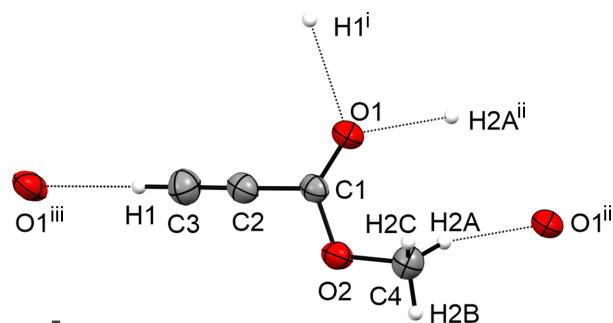
#### 3.1. Single-crystal X-ray diffraction

##### 3.1.1. Crystal structure of methyl prop-2-ynoate (**I**)

Compound **I** crystallizes in the monoclinic space group  $P2_1/n$  with one formula unit per unit cell. Fig. 4 displays the asymmetric unit. The C1–C2 bond length [1.4466 (15) Å] is significantly elongated compared to an average  $Csp^1-Csp^2$  hybridized bond (1.427 Å) determined by X-ray diffraction (Allen *et al.*, 1987). The C2≡C3 triple bond [1.1780 (16) Å] is in the same range as average terminal C≡C bonds (1.181 Å; Allen *et al.*, 1987). The C1=O1 bond [1.1972 (14) Å] is in the same range as other C=O bonds (1.196 Å) in esters (Allen *et al.*, 1987). The C1–O2 bond [1.3195 (12) Å] is significantly shortened compared to other esters (1.337 Å; Allen *et al.*, 1987). The C4–O2 bond [1.4463 (13) Å] is significantly elongated compared to average CH<sub>3</sub>–O bonds in esters (1.418 Å; Allen *et al.*, 1987).



**Figure 4**  
The asymmetric unit of **I**, with displacement ellipsoids drawn at the 50% probability level.



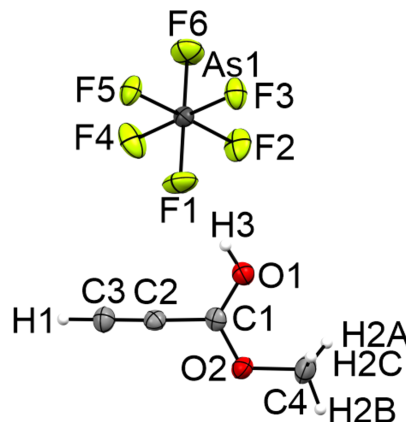
**Figure 5**  
Hydrogen bonds in the crystal structure of **I**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 2$ ; (iii)  $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ]

The crystal structure of **I** displays a layered structure built of weak C3–H1···O1 hydrogen bonds, according to the classification of Jeffrey (1997). The layered structure is connected *via* weak C4–H2A···O1 hydrogen bonds into a three-dimensional network (Fig. 5), according to the classification of Jeffrey (1997).

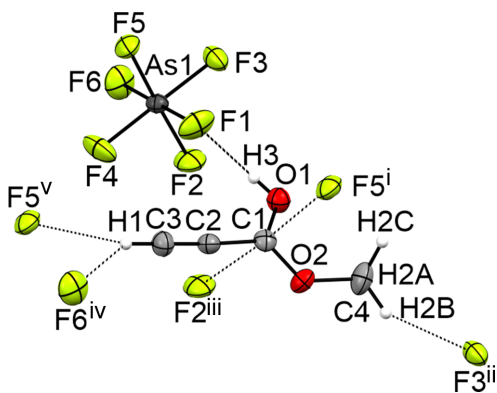
##### 3.1.2. Crystal structure of (1-methoxyprop-2-yn-1-ylidene) oxidanium hexafluoroarsenate (**III**)

Salt **III** crystallizes in the monoclinic space group  $P2_1/n$  with four formula units per unit cell. Fig. 6 displays the asymmetric unit of **III**. The C1–O1 bond [1.261 (4) Å] is significantly elongated by 0.064 Å due to the protonation compared to **I**. The C1–O2 bond [1.270 (3) Å] is significantly shortened by 0.049 Å compared to the starting material **I**. Due to the protonation, the C4–O2 bond [1.484 (4) Å] is elongated by 0.038 Å compared to the neutral compound **I**. The C2≡C3 triple bond is not significantly influenced by the protonation.

The three-dimensional network of **III** (Fig. 7) is built by a strong O1–H3···F1 and three weak C3–H1···F5, C3–H1···F6 and C4–H2B···F3 hydrogen bonds, according to the classification of Jeffrey (1997). Additionally, the crystal structure forms two interatomic contacts (C1···F2 and C1···F5) which are 8% shorter than the sum of the van der Waals radii.



**Figure 6**  
The asymmetric unit of **III**, with displacement ellipsoids drawn at the 50% probability level.


**Figure 7**

The intramolecular interactions in the crystal structure of **III**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x, -y + 1, -z + 1$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x, y - 1, z$ ; (v)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .]

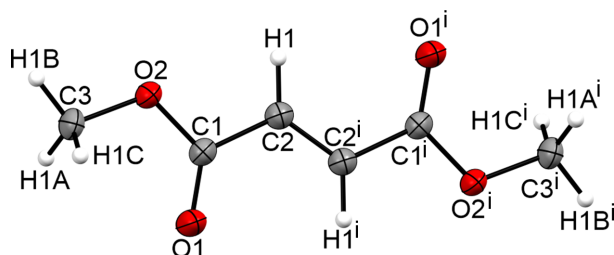
### 3.1.3. Crystal structure of dimethyl (*E*)-but-2-enedioate (**IV**)

The determined crystal structure is in the same range as that reported by Kooijman *et al.* (2004). The formula unit is shown in Fig. 8 and the crystal structure exhibits the same three-dimensional network (Fig. 9).

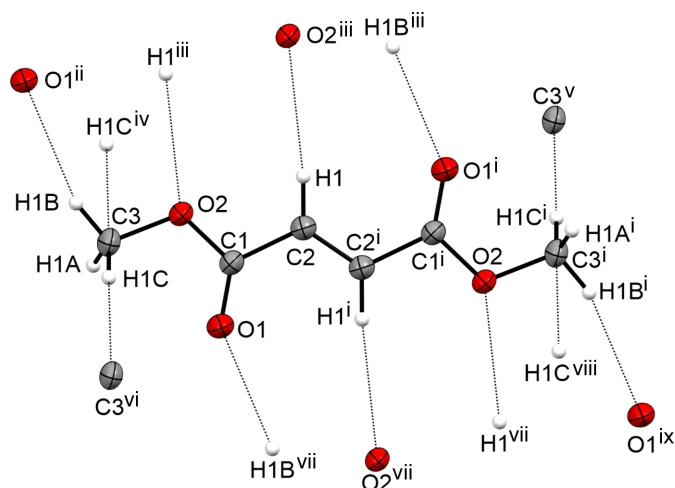
### 3.1.4. Crystal structure of 1,4-dimethoxy-4-oxobut-2-en-1-ylidene]oxidanium tetrafluoroborate–hydrogen fluoride (1/2) (**VI**)

The crystal structure of the monoprotonated species **VI** of dimethyl fumarate crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell. Fig. 10 displays the asymmetric unit. Similar to fumaric acid and acetylenedicarboxylic acid, the monoprotonated type forms extended chains of cations that are connected *via* strong O3–H9...O1 hydrogen bonds (Jessen & Kornath, 2022; Bayer *et al.*, 2020; Jeffrey, 1997). Due to the protonation, the C1–O1 [1.248 (3) Å] and C4–O3 [1.247 (3) Å] bonds are significantly elongated compared to the neutral compound [1.205 (2) Å]. The C1–O2 and C4–O4 bonds [both 1.289 (3) Å] are shortened by 0.052 Å compared to the starting material **IV**. The CH<sub>3</sub>–O and C2=C3 bonds are not significantly influenced by the monoprotonation.

Besides the strong hydrogen bonding between the cations, the crystal structure forms a medium–strong C6–H6...F6


**Figure 8**

The formula unit of **IV**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ .]

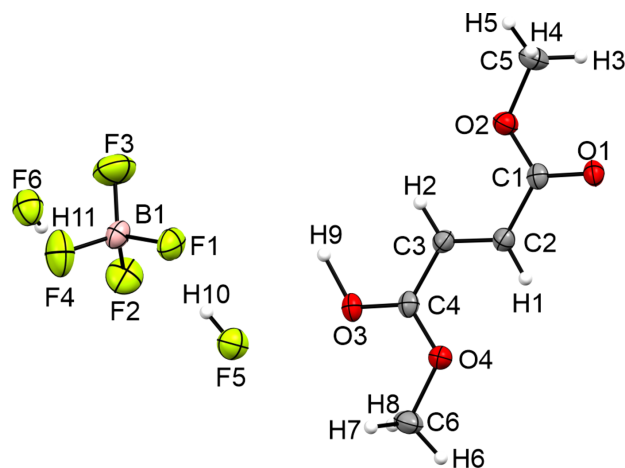

**Figure 9**

The intramolecular interactions in the crystal structure of **IV**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $x - 1, y - 1, z$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $x - 1, y, z$ ; (v)  $-x, -y + 2, -z + 1$ ; (vi)  $x + 1, y, z$ ; (vii)  $x + 1, y + 1, z$ ; (viii)  $-x + 2, -y + 2, -z + 1$ ; (ix)  $-x + 2, -y + 3, -z + 1$ .]

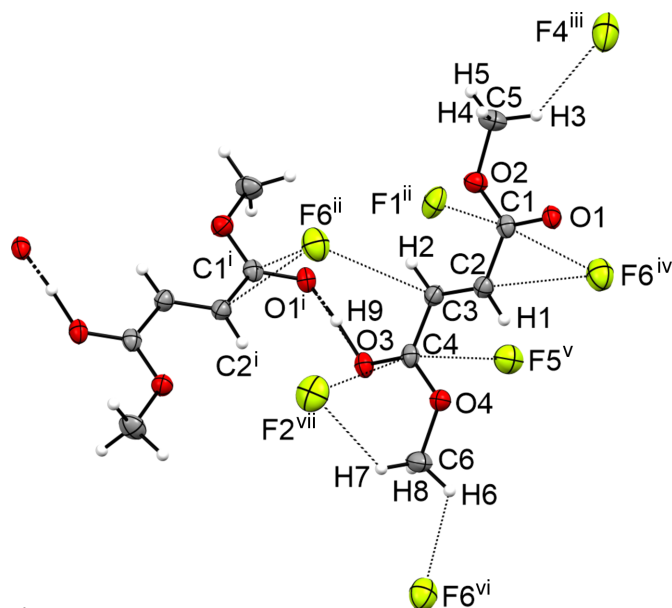
hydrogen bond [3.198 (3) Å] and two weak C5–H3...F4 [3.242 (3) Å] and C6–H7...F2 [3.261 (3) Å] hydrogen bonds. Furthermore, the crystal structure forms six interatomic C...F contacts, *i.e.* C1...F1 [2.900 (3) Å], C1...F6 [2.943 (3) Å], C2...F6 [2.987 (3) Å], C3...F6 [3.048 (3) Å], C4...F2 [3.020 (3) Å] and C4...F5 [2.974 (3) Å], which are shorter than the sum of the van der Waals radii (3.17 Å). The interactions in the crystal structure of **VI** are shown in Fig. 11.

### 3.1.5. Crystal structure of hemi[1,4-dimethoxy-4-oxidaniumylidenebut-2-en-1-ylidene]oxidanium} undecafluoroarsenate (**VII**)

The crystal structure of the diprotonated species **VII** of dimethyl fumarate crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell. Fig. 12 displays the formula unit. The crystal structure of the dipro-


**Figure 10**

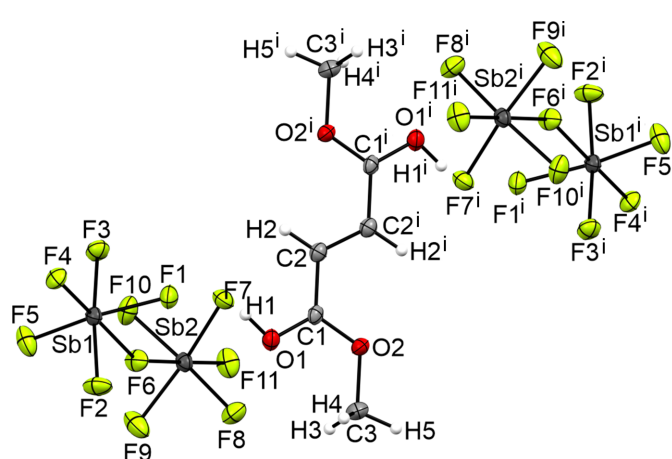
The asymmetric unit of **VI**, with displacement ellipsoids drawn at the 50% probability level.



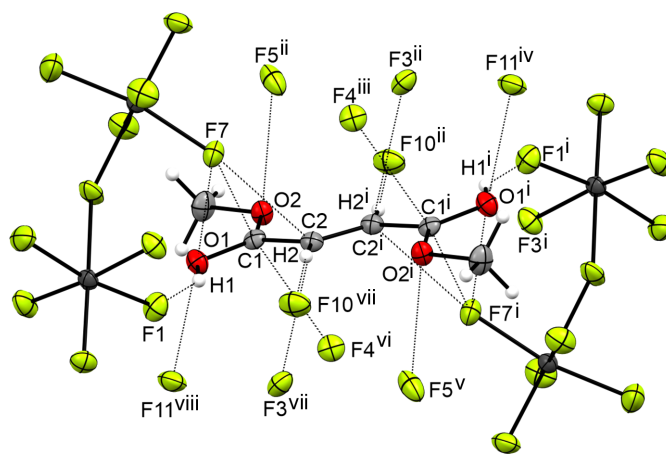
**Figure 11**  
The intramolecular interactions in the crystal structure of **VI**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (iii)  $x - \frac{1}{2}, y + 1, -z + \frac{1}{2}$ ; (iv)  $x, y + 1, z$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; (vi)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (vii)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .]

tonated species has a C1—O1 bond [1.277 (5) Å] significantly elongated by 0.072 Å compared to the starting material [1.205 (2) Å]. The C1—O2 bond [1.281 (5) Å] is shortened by 0.060 Å compared to the neutral compound [1.341 (1) Å]. The C3—O2 bond [1.489 (6) Å] is elongated by 0.034 Å compared to **IV** [1.455 (2) Å].

The three-dimensional network is formed by a strong O1—H1···F1 hydrogen bond and seven interatomic interactions (Jeffrey, 1997). The interatomic interactions are C1···F4 [3.061 (4) Å], C1···F7 [3.001 (4) Å], C2···F3 [2.958 (5) Å], C2···F7 [3.008 (5) Å], C3···F2 [3.050 (6) Å], O1···F7 [2.985 (4) Å] and O1···F11 [2.864 (4) Å]. Fig. 13 displays the interatomic distances in the crystal structure of **VII**.



**Figure 12**  
The formula unit of **VIII**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

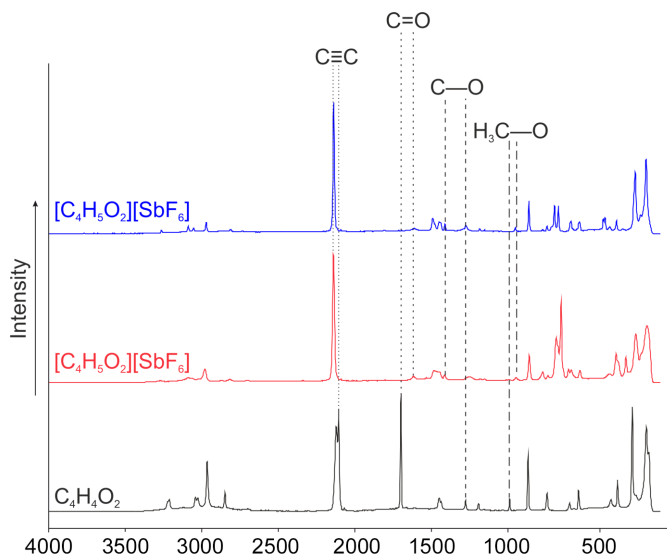


**Figure 13**  
The intramolecular interactions in the crystal structure of **VIII**, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + \frac{3}{2}, y + \frac{1}{2}, z$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (iv)  $-x + 2, -y + 1, -z + 1$ ; (v)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (vi)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (vii)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (viii)  $x - 1, y, z$ .]

## 3.2. Raman spectroscopy

### 3.2.1. Raman spectra of **I**, **II** and **III**

Fig. 14 displays the low-temperature Raman spectra of **I**, **II** and **III**. The first evidence for successful protonation is the significantly red-shifted C=O oscillation from 1700  $\text{cm}^{-1}$  in the starting material **I** to 1617 (in **II**) and 1615  $\text{cm}^{-1}$  (in **III**). Due to the protonation, the C—O oscillation is blue-shifted in the Raman spectra to 1414 (in **II**) and 1413  $\text{cm}^{-1}$  (in **III**) compared to the starting material (1278  $\text{cm}^{-1}$ ). The H<sub>3</sub>C—O oscillation is red-shifted by 42  $\text{cm}^{-1}$  to 948 (in **II**) and 951  $\text{cm}^{-1}$  (in **III**) compared to **I** (990  $\text{cm}^{-1}$ ). The oscillation of the triple bond is only slightly affected from 2107  $\text{cm}^{-1}$  to 2141 (in **II**) and 2140  $\text{cm}^{-1}$  (in **III**).



**Figure 14**  
The low-temperature Raman spectra of **I** (black), **II** (red) and **III** (blue).

### 3.2.2. Raman spectra of IV, V, VII and VIII

Fig. 15 shows the low-temperature Raman spectra of **IV**, **V**, **VII** and **VIII**. The C=O oscillation is red-shifted by  $48\text{ cm}^{-1}$  to  $1611\text{ cm}^{-1}$  compared to **IV** ( $1659\text{ cm}^{-1}$ ). Due to the protonation, the C–O oscillation is blue-shifted in the Raman spectra to  $1401\text{ cm}^{-1}$  (**V**) compared to the neutral compound ( $1217\text{ cm}^{-1}$ ). The C=C oscillation is only slightly red shifted to  $1705\text{ cm}^{-1}$  compared to the starting material ( $1725\text{ cm}^{-1}$ ).

The diprotonation is characterized by a red-shifted C=O oscillation by  $46\text{ cm}^{-1}$  to  $1613\text{ cm}^{-1}$  in the spectra of **VII** and **VIII** compared to the Raman spectrum of **IV** ( $1659\text{ cm}^{-1}$ ). The C=C oscillation is significantly red-shifted by  $38\text{ cm}^{-1}$  to  $1686\text{ cm}^{-1}$  in the spectra of **VII** and **VIII** compared to the Raman spectrum of **IV** ( $1724\text{ cm}^{-1}$ ). Due to the protonation, the C–O oscillation is blue-shifted in the Raman spectra to  $1419\text{ cm}^{-1}$  (in **VII**) and  $1425\text{ cm}^{-1}$  (in **VIII**) compared to the neutral compound ( $1217\text{ cm}^{-1}$ ).

## 4. Conclusion

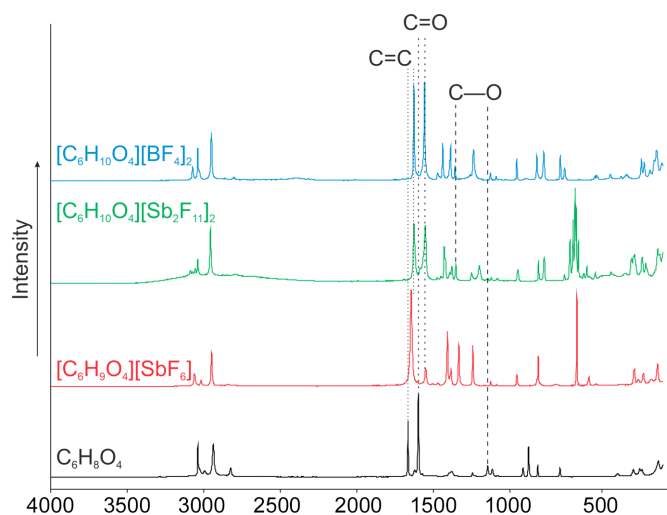
We present herein the first single-crystal X-ray diffraction and Raman spectroscopy study of the monoprotonated species of methyl prop-2-ynoate and mono- and diprotonated species of dimethyl fumarate. All three protonated species crystallize in the more stable *syn-anti* conformation. Furthermore, the first single-crystal structure of methyl prop-2-ynoate is reported. The protonated species are important intermediates of acid-catalyzed reactions.

## Acknowledgements

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**Figure 15**  
The low-temperature Raman spectra of **IV** (black), **V** (red), **VII** (green) and **VIII** (blue).

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## supporting information

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## The crystal structures of methyl prop-2-ynoate, dimethyl fumarate and their protonated species

**Dirk Hollenwäger, Valentin Bockmair and Andreas J. Kornath**

### Computing details

#### Methyl prop-2-ynoate (I)

##### Crystal data

$C_4H_4O_2$

$M_r = 84.07$

Monoclinic,  $P2_1/n$

$a = 3.8409$  (5) Å

$b = 15.593$  (2) Å

$c = 7.6149$  (10) Å

$\beta = 99.910$  (12)°

$V = 449.27$  (10) Å<sup>3</sup>

$Z = 4$

$F(000) = 176$

$D_x = 1.243$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1269 reflections

$\theta = 3.0\text{--}31.5^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 111$  K

Needle, colorless

$1.00 \times 0.56 \times 0.31$  mm

##### Data collection

Rigaku Xcalibur Sapphire3  
diffractometer

Radiation source: Enhance (Mo) X-ray Source  
Graphite monochromator

Detector resolution: 15.9809 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(CrysAlis PRO; Rigaku OD, 2020)

$T_{\min} = 0.457$ ,  $T_{\max} = 1.000$

3885 measured reflections

1060 independent reflections

891 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.9^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -5 \rightarrow 5$

$k = -12 \rightarrow 20$

$l = -10 \rightarrow 10$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.099$

$S = 1.05$

1060 reflections

71 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.0483P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.15$  e Å<sup>-3</sup>



*Special details*

**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.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.31342 (18)	0.52742 (5)	0.65891 (10)	0.0344 (2)
O1	0.1276 (2)	0.59990 (5)	0.87804 (11)	0.0450 (3)
C1	0.2479 (3)	0.59799 (6)	0.74312 (14)	0.0293 (3)
C2	0.3393 (3)	0.67347 (7)	0.65039 (14)	0.0350 (3)
C4	0.2276 (3)	0.44773 (8)	0.73879 (18)	0.0383 (3)
C3	0.4129 (3)	0.73534 (8)	0.57592 (18)	0.0440 (3)
H1	0.470 (4)	0.7836 (9)	0.517 (2)	0.058 (4)*
H2B	0.295 (4)	0.4053 (9)	0.664 (2)	0.061 (5)*
H2A	0.363 (4)	0.4414 (9)	0.853 (2)	0.057 (4)*
H2C	-0.013 (4)	0.4444 (9)	0.741 (2)	0.061 (4)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O2	0.0382 (4)	0.0368 (4)	0.0295 (4)	-0.0001 (3)	0.0097 (3)	-0.0030 (3)
O1	0.0635 (6)	0.0427 (5)	0.0340 (5)	0.0123 (4)	0.0229 (4)	0.0042 (3)
C1	0.0265 (5)	0.0361 (6)	0.0249 (5)	0.0037 (4)	0.0031 (4)	0.0007 (4)
C2	0.0328 (5)	0.0416 (6)	0.0308 (6)	0.0017 (4)	0.0064 (4)	-0.0010 (4)
C4	0.0390 (6)	0.0356 (6)	0.0398 (7)	0.0007 (4)	0.0056 (5)	0.0014 (5)
C3	0.0465 (7)	0.0409 (6)	0.0462 (7)	-0.0022 (5)	0.0124 (5)	0.0041 (5)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

O2—C1	1.3195 (12)	C1—C2	1.4466 (15)
O2—C4	1.4463 (13)	C2—C3	1.1780 (16)
O1—C1	1.1972 (14)		
C1—O2—C4	115.83 (9)	O2—C1—C2	111.02 (9)
O1—C1—O2	124.88 (10)	C3—C2—C1	179.47 (11)
O1—C1—C2	124.10 (10)		
C4—O2—C1—O1	0.50 (16)	C4—O2—C1—C2	-179.25 (9)

(1-Methoxyprop-2-yn-1-ylidene)oxidanium hexafluoroarsenate (III)

Crystal data

$C_4H_5O_2^+ \cdot AsF_6^-$	$F(000) = 528$
$M_r = 274.00$	$D_x = 2.135 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.9609 (5) \text{ \AA}$	Cell parameters from 1298 reflections
$b = 8.9319 (7) \text{ \AA}$	$\theta = 2.3\text{--}31.5^\circ$
$c = 13.7189 (9) \text{ \AA}$	$\mu = 4.06 \text{ mm}^{-1}$
$\beta = 91.664 (7)^\circ$	$T = 111 \text{ K}$
$V = 852.60 (11) \text{ \AA}^3$	Needle, colorless
$Z = 4$	$0.90 \times 0.21 \times 0.15 \text{ mm}$

Data collection

Rigaku Xcalibur Sapphire3 diffractometer	4205 measured reflections
Radiation source: Enhance (Mo) X-ray Source	2303 independent reflections
Graphite monochromator	1900 reflections with $I > 2\sigma(I)$
Detector resolution: $15.9809 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.029$
$\omega$ scans	$\theta_{\text{max}} = 29.1^\circ$ , $\theta_{\text{min}} = 2.7^\circ$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2020)	$h = -6 \rightarrow 9$
$T_{\text{min}} = 0.582$ , $T_{\text{max}} = 1.000$	$k = -9 \rightarrow 12$
	$l = -18 \rightarrow 18$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2303 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
123 parameters	$\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.92 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

**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.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.55531 (4)	0.61946 (4)	0.31141 (2)	0.02340 (12)
F3	0.3663 (2)	0.7351 (3)	0.28285 (13)	0.0380 (5)
F5	0.5944 (3)	0.5983 (2)	0.18954 (13)	0.0380 (5)
F2	0.5053 (3)	0.6364 (3)	0.43228 (14)	0.0462 (6)

O2	0.0897 (3)	0.1533 (3)	0.50117 (16)	0.0301 (5)
O1	0.1633 (3)	0.3569 (3)	0.42071 (18)	0.0310 (5)
F4	0.7411 (3)	0.5020 (3)	0.33987 (16)	0.0503 (6)
F1	0.3982 (3)	0.4674 (3)	0.30251 (16)	0.0508 (6)
F6	0.7072 (3)	0.7683 (3)	0.31930 (17)	0.0496 (6)
C1	0.1973 (4)	0.2223 (4)	0.44299 (19)	0.0244 (6)
C2	0.3535 (4)	0.1383 (4)	0.4053 (2)	0.0256 (6)
C3	0.4795 (4)	0.0709 (4)	0.3697 (2)	0.0323 (7)
H1	0.580815	0.016719	0.341095	0.039*
C4	-0.0767 (4)	0.2351 (5)	0.5405 (3)	0.0417 (9)
H2A	-0.030985	0.324746	0.575262	0.063*
H2B	-0.144696	0.170089	0.585530	0.063*
H2C	-0.164273	0.264647	0.486657	0.063*
H3	0.235 (6)	0.394 (5)	0.387 (3)	0.047 (13)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
As1	0.02680 (18)	0.0244 (2)	0.01897 (17)	0.00042 (12)	-0.00046 (12)	0.00004 (12)
F3	0.0363 (9)	0.0460 (13)	0.0313 (9)	0.0157 (10)	-0.0033 (8)	-0.0030 (10)
F5	0.0382 (10)	0.0531 (14)	0.0230 (9)	0.0054 (9)	0.0071 (8)	-0.0007 (9)
F2	0.0596 (13)	0.0605 (16)	0.0187 (8)	0.0094 (11)	0.0016 (9)	-0.0008 (10)
O2	0.0335 (11)	0.0311 (13)	0.0260 (10)	-0.0035 (10)	0.0083 (9)	-0.0020 (10)
O1	0.0305 (11)	0.0281 (13)	0.0344 (12)	0.0014 (10)	0.0023 (10)	-0.0015 (11)
F4	0.0579 (12)	0.0450 (14)	0.0469 (12)	0.0253 (11)	-0.0158 (10)	-0.0018 (11)
F1	0.0657 (14)	0.0441 (14)	0.0430 (12)	-0.0300 (12)	0.0066 (10)	-0.0002 (11)
F6	0.0425 (11)	0.0429 (14)	0.0631 (14)	-0.0170 (10)	-0.0034 (10)	-0.0051 (13)
C1	0.0251 (13)	0.0279 (17)	0.0200 (13)	-0.0020 (12)	-0.0033 (11)	-0.0057 (13)
C2	0.0283 (14)	0.0260 (17)	0.0226 (13)	0.0005 (12)	0.0000 (11)	0.0028 (13)
C3	0.0292 (14)	0.0346 (19)	0.0333 (16)	0.0049 (14)	0.0032 (12)	-0.0012 (15)
C4	0.0339 (16)	0.049 (2)	0.0436 (19)	-0.0021 (17)	0.0149 (15)	-0.0097 (19)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

As1—F6	1.700 (2)	O2—C1	1.270 (3)
As1—F4	1.702 (2)	O2—C4	1.484 (4)
As1—F3	1.7091 (19)	O1—C1	1.261 (4)
As1—F2	1.7109 (19)	C1—C2	1.430 (4)
As1—F5	1.7122 (18)	C2—C3	1.180 (4)
As1—F1	1.746 (2)		
F6—As1—F4	90.03 (12)	F6—As1—F1	179.51 (12)
F6—As1—F3	90.88 (11)	F4—As1—F1	90.37 (13)
F4—As1—F3	179.09 (11)	F3—As1—F1	88.72 (12)
F6—As1—F2	90.72 (11)	F2—As1—F1	89.55 (11)
F4—As1—F2	90.39 (11)	F5—As1—F1	87.85 (10)
F3—As1—F2	89.53 (10)	C1—O2—C4	118.0 (3)
F6—As1—F5	91.87 (11)	O1—C1—O2	120.3 (3)

F4—As1—F5	90.84 (10)	O1—C1—C2	123.4 (3)
F3—As1—F5	89.20 (9)	O2—C1—C2	116.2 (3)
F2—As1—F5	177.13 (10)	C3—C2—C1	176.8 (3)
C4—O2—C1—O1	0.8 (4)	C4—O2—C1—C2	−178.7 (3)

**Dimethyl (*E*)-but-2-enedioate (IV)***Crystal data*C<sub>6</sub>H<sub>8</sub>O<sub>4</sub> $M_r = 144.12$ Triclinic,  $P\bar{1}$  $a = 3.8726$  (11) Å $b = 5.6546$  (10) Å $c = 8.3778$  (18) Å $\alpha = 100.642$  (16)° $\beta = 100.42$  (2)° $\gamma = 105.73$  (2)° $V = 168.30$  (7) Å<sup>3</sup> $Z = 1$  $F(000) = 76$  $D_x = 1.422$  Mg m<sup>−3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 712 reflections

 $\theta = 3.9$ – $32.0$ ° $\mu = 0.12$  mm<sup>−1</sup> $T = 112$  K

Plate, colorless

 $0.52 \times 0.46 \times 0.35$  mm*Data collection*Rigaku Xcalibur Sapphire3  
diffractometerRadiation source: Enhance (Mo) X-ray Source  
Graphite monochromatorDetector resolution: 15.9809 pixels mm<sup>−1</sup> $\omega$  scansAbsorption correction: multi-scan  
(CrysAlis PRO; Rigaku OD, 2020) $T_{\min} = 0.579$ ,  $T_{\max} = 1.000$ 

1403 measured reflections

825 independent reflections

703 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.015$  $\theta_{\text{max}} = 28.3$ °,  $\theta_{\text{min}} = 4.1$ ° $h = -5 \rightarrow 5$  $k = -5 \rightarrow 7$  $l = -10 \rightarrow 11$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.048$  $wR(F^2) = 0.144$  $S = 1.04$ 

825 reflections

51 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.1042P)^2 + 0.0039P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.52$  e Å<sup>−3</sup> $\Delta\rho_{\text{min}} = -0.24$  e Å<sup>−3</sup>*Special details*

**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.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.2058 (2)	0.46773 (15)	0.30549 (11)	0.0270 (3)
O1	0.5682 (3)	0.77635 (18)	0.21852 (12)	0.0381 (4)
C2	0.3998 (3)	0.8781 (2)	0.47844 (15)	0.0244 (4)
C1	0.4062 (3)	0.7084 (2)	0.32036 (14)	0.0237 (4)
C3	0.1927 (4)	0.2863 (2)	0.15494 (16)	0.0295 (4)
H1A	0.078071	0.332324	0.056057	0.044*
H1B	0.046722	0.116090	0.156867	0.044*
H1C	0.444625	0.288310	0.150486	0.044*
H1	0.246 (5)	0.796 (3)	0.544 (2)	0.034 (4)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O2	0.0328 (5)	0.0188 (5)	0.0261 (5)	0.0011 (4)	0.0112 (4)	0.0039 (4)
O1	0.0484 (6)	0.0260 (6)	0.0335 (6)	−0.0030 (4)	0.0210 (5)	0.0035 (4)
C2	0.0249 (6)	0.0231 (7)	0.0238 (6)	0.0045 (5)	0.0075 (4)	0.0056 (5)
C1	0.0235 (6)	0.0206 (6)	0.0242 (6)	0.0027 (5)	0.0059 (4)	0.0048 (5)
C3	0.0354 (7)	0.0197 (6)	0.0278 (7)	0.0028 (5)	0.0086 (5)	0.0006 (5)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O2—C1	1.3414 (14)	C2—C2 <sup>i</sup>	1.329 (2)
O2—C3	1.4549 (14)	C2—C1	1.4937 (17)
O1—C1	1.2055 (15)		
C1—O2—C3	115.47 (9)	O1—C1—C2	125.05 (11)
C2 <sup>i</sup> —C2—C1	120.37 (14)	O2—C1—C2	111.03 (11)
O1—C1—O2	123.92 (11)		
C3—O2—C1—O1	−0.07 (19)	C2 <sup>i</sup> —C2—C1—O1	−4.2 (2)
C3—O2—C1—C2	179.80 (9)	C2 <sup>i</sup> —C2—C1—O2	175.91 (13)

Symmetry code: (i)  $-x+1, -y+2, -z+1$ .

1,4-Dimethoxy-4-oxobut-2-en-1-ylidene]oxidanium tetrafluoroborate–hydrogen fluoride (1/2) (VI)

Crystal data

$\text{C}_6\text{H}_9\text{O}_4^+ \cdot \text{BF}_4^- \cdot 2\text{HF}$   
 $M_r = 271.96$   
 Orthorhombic, *Pbca*  
 $a = 12.8759$  (5)  $\text{\AA}$   
 $b = 11.8899$  (4)  $\text{\AA}$   
 $c = 14.6252$  (7)  $\text{\AA}$   
 $V = 2239.02$  (16)  $\text{\AA}^3$   
 $Z = 8$   
 $F(000) = 1104$

$D_x = 1.614$   $\text{Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$   
 Cell parameters from 2510 reflections  
 $\theta = 2.7\text{--}31.9^\circ$   
 $\mu = 0.19$   $\text{mm}^{-1}$   
 $T = 101$  K  
 Plate, colorless  
 $0.28 \times 0.18 \times 0.11$  mm

Data collection

Rigaku Xcalibur Sapphire3 diffractometer	7514 measured reflections
Radiation source: Enhance (Mo) X-ray Source	1717 independent reflections
Graphite monochromator	1478 reflections with $I > 2\sigma(I)$
Detector resolution: 15.9809 pixels mm <sup>-1</sup>	$R_{\text{int}} = 0.026$
$\omega$ scans	$\theta_{\text{max}} = 23.8^\circ$ , $\theta_{\text{min}} = 2.7^\circ$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2020)	$h = -14 \rightarrow 11$
$T_{\text{min}} = 0.885$ , $T_{\text{max}} = 1.000$	$k = -13 \rightarrow 6$
	$l = -16 \rightarrow 16$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 2.1459P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
1717 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
176 parameters	$\Delta\rho_{\text{max}} = 0.77 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

**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.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.52277 (12)	0.16806 (12)	0.38516 (10)	0.0424 (4)
F5	0.50136 (12)	0.27683 (13)	0.53107 (11)	0.0415 (4)
O4	0.32442 (12)	0.62198 (12)	0.58784 (10)	0.0255 (4)
O1	0.13464 (12)	0.86421 (12)	0.36669 (10)	0.0249 (4)
O3	0.36950 (12)	0.47179 (12)	0.50843 (11)	0.0256 (4)
O2	0.18127 (12)	0.71387 (13)	0.28735 (10)	0.0275 (4)
F6	0.36144 (13)	-0.08191 (13)	0.38730 (12)	0.0467 (4)
F2	0.68532 (12)	0.09644 (14)	0.38787 (12)	0.0525 (5)
F4	0.54899 (14)	-0.01889 (13)	0.39813 (14)	0.0598 (5)
F3	0.58307 (16)	0.06993 (16)	0.26486 (12)	0.0681 (6)
C4	0.32631 (17)	0.56549 (18)	0.51262 (15)	0.0223 (5)
C2	0.23256 (17)	0.71960 (18)	0.44011 (16)	0.0229 (5)
C1	0.17955 (17)	0.77141 (18)	0.36205 (15)	0.0222 (5)
C3	0.27536 (18)	0.61916 (19)	0.43439 (15)	0.0232 (5)
C6	0.3732 (2)	0.5736 (2)	0.66902 (16)	0.0340 (6)
H7	0.332494	0.508833	0.689926	0.051*

H6	0.375883	0.630283	0.717592	0.051*
H8	0.443830	0.549154	0.653995	0.051*
C5	0.1229 (2)	0.7558 (2)	0.20841 (16)	0.0328 (6)
H4	0.048343	0.747717	0.219943	0.049*
H5	0.141976	0.712458	0.153940	0.049*
H3	0.139489	0.835347	0.198520	0.049*
B1	0.5867 (2)	0.0793 (2)	0.35695 (19)	0.0294 (6)
H2	0.2735 (18)	0.5775 (19)	0.3809 (16)	0.025 (6)*
H1	0.2311 (19)	0.758 (2)	0.4951 (17)	0.030 (6)*
H10	0.509 (3)	0.231 (3)	0.485 (3)	0.088 (14)*
H11	0.425 (3)	-0.056 (3)	0.396 (3)	0.088 (13)*
H9	0.363 (3)	0.421 (2)	0.4363 (11)	0.101 (13)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
F1	0.0422 (9)	0.0355 (8)	0.0493 (9)	0.0150 (7)	-0.0058 (7)	-0.0100 (7)
F5	0.0399 (9)	0.0439 (9)	0.0408 (9)	0.0092 (7)	0.0031 (7)	-0.0027 (7)
O4	0.0301 (9)	0.0235 (8)	0.0231 (9)	0.0014 (7)	-0.0017 (7)	-0.0002 (7)
O1	0.0253 (9)	0.0184 (8)	0.0311 (9)	0.0009 (7)	-0.0025 (7)	0.0018 (7)
O3	0.0245 (9)	0.0187 (8)	0.0336 (9)	0.0026 (7)	0.0009 (7)	0.0017 (7)
O2	0.0305 (9)	0.0290 (9)	0.0231 (8)	0.0060 (7)	-0.0015 (7)	0.0002 (7)
F6	0.0404 (10)	0.0405 (9)	0.0593 (11)	-0.0046 (8)	-0.0029 (8)	0.0040 (8)
F2	0.0313 (9)	0.0594 (11)	0.0667 (11)	0.0051 (8)	-0.0063 (8)	-0.0041 (9)
F4	0.0510 (11)	0.0370 (9)	0.0915 (14)	-0.0035 (8)	0.0098 (10)	0.0054 (9)
F3	0.0852 (14)	0.0799 (13)	0.0393 (10)	0.0153 (11)	-0.0028 (9)	-0.0159 (9)
C4	0.0189 (11)	0.0191 (12)	0.0289 (13)	-0.0028 (10)	0.0013 (9)	0.0006 (10)
C2	0.0241 (12)	0.0216 (12)	0.0231 (12)	-0.0011 (10)	0.0019 (10)	-0.0014 (10)
C1	0.0182 (11)	0.0207 (12)	0.0277 (12)	-0.0020 (10)	0.0012 (9)	0.0012 (10)
C3	0.0253 (12)	0.0210 (11)	0.0234 (12)	-0.0016 (10)	-0.0002 (10)	-0.0027 (10)
C6	0.0383 (15)	0.0376 (14)	0.0261 (13)	-0.0023 (12)	-0.0086 (11)	0.0054 (11)
C5	0.0348 (14)	0.0400 (14)	0.0238 (12)	0.0042 (12)	-0.0042 (11)	0.0049 (11)
B1	0.0270 (15)	0.0262 (14)	0.0349 (16)	0.0014 (12)	0.0013 (12)	-0.0065 (12)

*Geometric parameters (Å, °)*

F1—B1	1.401 (3)	F2—B1	1.363 (3)
O4—C4	1.289 (3)	F4—B1	1.401 (3)
O4—C6	1.461 (3)	F3—B1	1.352 (3)
O1—C1	1.247 (3)	C4—C3	1.465 (3)
O3—C4	1.247 (3)	C2—C3	1.318 (3)
O2—C1	1.289 (3)	C2—C1	1.466 (3)
O2—C5	1.465 (3)		
C4—O4—C6	118.69 (18)	O2—C1—C2	115.41 (19)
C1—O2—C5	118.59 (17)	C2—C3—C4	122.2 (2)
O3—C4—O4	121.1 (2)	F3—B1—F2	112.1 (2)
O3—C4—C3	123.4 (2)	F3—B1—F1	109.6 (2)

O4—C4—C3	115.54 (19)	F2—B1—F1	109.7 (2)
C3—C2—C1	121.7 (2)	F3—B1—F4	110.3 (2)
O1—C1—O2	121.6 (2)	F2—B1—F4	107.8 (2)
O1—C1—C2	123.0 (2)	F1—B1—F4	107.3 (2)
C6—O4—C4—O3	−0.6 (3)	C3—C2—C1—O2	−2.4 (3)
C6—O4—C4—C3	179.66 (19)	C1—C2—C3—C4	−178.5 (2)
C5—O2—C1—O1	−4.1 (3)	O3—C4—C3—C2	−178.2 (2)
C5—O2—C1—C2	175.19 (19)	O4—C4—C3—C2	1.5 (3)
C3—C2—C1—O1	176.9 (2)		

Hemi{[1,4-dimethoxy-4-oxidaniumylidenebut-2-en-1-ylidene]oxidanium} undecafluorodiarsenate (VII)

*Crystal data*

$0.5\text{C}_6\text{H}_{10}\text{O}_4^{2+} \cdot \text{Sb}_2\text{F}_{11}^-$

$M_r = 525.57$

Orthorhombic, *Pbca*

$a = 7.8461$  (6) Å

$b = 15.1531$  (11) Å

$c = 19.5536$  (17) Å

$V = 2324.8$  (3) Å<sup>3</sup>

$Z = 8$

$F(000) = 1920$

$D_x = 3.003$  Mg m<sup>−3</sup>

Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3099 reflections

$\theta = 3.1\text{--}31.4^\circ$

$\mu = 4.79$  mm<sup>−1</sup>

$T = 101$  K

Needle, colorless

$0.25 \times 0.11 \times 0.05$  mm

*Data collection*

Rigaku Xcalibur Sapphire3

diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 15.9809 pixels mm<sup>−1</sup>

$\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2020)

$T_{\min} = 0.807$ ,  $T_{\max} = 1.000$

13316 measured reflections

3784 independent reflections

2878 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 32.2^\circ$ ,  $\theta_{\min} = 2.9^\circ$

$h = -11 \rightarrow 11$

$k = -22 \rightarrow 18$

$l = -19 \rightarrow 29$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.071$

$S = 1.04$

3784 reflections

169 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.021P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 1.09$  e Å<sup>−3</sup>

$\Delta\rho_{\min} = -1.01$  e Å<sup>−3</sup>

*Special details*

**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.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Sb1	0.53289 (3)	0.11951 (2)	0.58884 (2)	0.01838 (7)
Sb2	0.87980 (3)	0.29435 (2)	0.64518 (2)	0.01906 (8)
F6	0.6878 (3)	0.20173 (15)	0.64187 (14)	0.0290 (6)
F4	0.3807 (3)	0.04618 (14)	0.54353 (14)	0.0254 (6)
F11	1.0501 (3)	0.37949 (16)	0.64744 (16)	0.0325 (7)
F7	0.7631 (3)	0.34255 (15)	0.57101 (14)	0.0267 (6)
F1	0.4121 (3)	0.22282 (15)	0.56555 (15)	0.0288 (6)
F8	0.7357 (3)	0.35628 (15)	0.70374 (15)	0.0313 (6)
F2	0.4096 (4)	0.11295 (17)	0.66985 (15)	0.0331 (6)
F3	0.6723 (3)	0.13957 (15)	0.51323 (14)	0.0278 (6)
O2	0.4521 (4)	0.52155 (17)	0.62437 (16)	0.0208 (6)
F5	0.6789 (3)	0.03114 (16)	0.61891 (17)	0.0360 (7)
F10	0.9958 (3)	0.21939 (16)	0.58552 (17)	0.0348 (7)
F9	0.9623 (4)	0.23004 (17)	0.71862 (17)	0.0414 (8)
O1	0.4065 (4)	0.37941 (18)	0.61581 (18)	0.0226 (6)
H1	0.400397	0.339397	0.586174	0.034*
C1	0.4470 (5)	0.4521 (2)	0.5871 (2)	0.0175 (8)
C3	0.4204 (6)	0.5136 (3)	0.6992 (3)	0.0283 (10)
H4	0.312992	0.482094	0.706860	0.043*
H5	0.413086	0.572665	0.719463	0.043*
H3	0.514077	0.480919	0.720535	0.043*
C2	0.4888 (5)	0.4604 (3)	0.5143 (2)	0.0189 (9)
H2	0.498 (5)	0.410 (3)	0.488 (2)	0.006 (10)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb1	0.02181 (13)	0.01431 (12)	0.01902 (15)	-0.00328 (10)	-0.00136 (11)	0.00006 (12)
Sb2	0.02106 (13)	0.01545 (12)	0.02066 (16)	-0.00268 (10)	-0.00279 (11)	0.00125 (12)
F6	0.0361 (14)	0.0251 (12)	0.0258 (16)	-0.0164 (10)	-0.0012 (12)	-0.0014 (12)
F4	0.0274 (13)	0.0227 (11)	0.0260 (15)	-0.0048 (9)	-0.0033 (11)	-0.0063 (12)
F11	0.0221 (13)	0.0275 (13)	0.048 (2)	-0.0080 (10)	-0.0049 (13)	0.0029 (13)
F7	0.0308 (14)	0.0278 (12)	0.0213 (15)	0.0027 (10)	-0.0024 (11)	0.0062 (12)
F1	0.0360 (15)	0.0194 (12)	0.0311 (17)	0.0062 (10)	-0.0033 (12)	-0.0022 (12)
F8	0.0339 (15)	0.0317 (12)	0.0283 (16)	-0.0049 (11)	0.0051 (12)	-0.0102 (13)
F2	0.0389 (16)	0.0416 (15)	0.0189 (15)	-0.0156 (12)	0.0049 (12)	0.0013 (13)
F3	0.0304 (14)	0.0282 (12)	0.0247 (15)	-0.0035 (10)	0.0094 (11)	-0.0026 (12)
O2	0.0278 (15)	0.0178 (13)	0.0169 (16)	-0.0014 (11)	0.0022 (13)	-0.0029 (13)
F5	0.0330 (14)	0.0241 (12)	0.051 (2)	-0.0011 (10)	-0.0142 (15)	0.0103 (14)
F10	0.0333 (15)	0.0254 (13)	0.046 (2)	0.0047 (10)	0.0046 (13)	-0.0071 (13)

F9	0.0490 (18)	0.0352 (15)	0.040 (2)	-0.0077 (13)	-0.0171 (15)	0.0145 (15)
O1	0.0253 (15)	0.0161 (13)	0.0263 (18)	0.0005 (11)	0.0040 (13)	-0.0002 (13)
C1	0.0161 (18)	0.0158 (17)	0.021 (2)	0.0045 (14)	-0.0015 (16)	-0.0022 (18)
C3	0.041 (3)	0.027 (2)	0.017 (2)	0.0022 (18)	0.001 (2)	-0.004 (2)
C2	0.0175 (19)	0.0186 (18)	0.021 (2)	0.0007 (14)	0.0006 (16)	-0.0020 (18)

*Geometric parameters (Å, °)*

Sb1—F4	1.856 (2)	Sb2—F7	1.864 (3)
Sb1—F5	1.858 (2)	Sb2—F10	1.865 (3)
Sb1—F2	1.859 (3)	Sb2—F6	2.060 (2)
Sb1—F3	1.864 (3)	O2—C1	1.281 (5)
Sb1—F1	1.886 (2)	O2—C3	1.489 (6)
Sb1—F6	2.026 (2)	O1—C1	1.277 (5)
Sb2—F9	1.852 (3)	C1—C2	1.466 (6)
Sb2—F11	1.858 (2)	C2—C2 <sup>i</sup>	1.334 (8)
Sb2—F8	1.863 (3)		
F4—Sb1—F5	96.68 (11)	F9—Sb2—F7	168.79 (11)
F4—Sb1—F2	92.29 (12)	F11—Sb2—F7	95.72 (12)
F5—Sb1—F2	90.73 (14)	F8—Sb2—F7	89.00 (12)
F4—Sb1—F3	95.54 (11)	F9—Sb2—F10	89.65 (14)
F5—Sb1—F3	90.38 (13)	F11—Sb2—F10	94.98 (12)
F2—Sb1—F3	171.91 (11)	F8—Sb2—F10	170.88 (11)
F4—Sb1—F1	93.34 (11)	F7—Sb2—F10	89.53 (13)
F5—Sb1—F1	169.97 (12)	F9—Sb2—F6	85.50 (11)
F2—Sb1—F1	89.34 (12)	F11—Sb2—F6	178.88 (11)
F3—Sb1—F1	88.18 (12)	F8—Sb2—F6	85.34 (11)
F4—Sb1—F6	176.70 (11)	F7—Sb2—F6	83.29 (11)
F5—Sb1—F6	84.91 (11)	F10—Sb2—F6	85.55 (11)
F2—Sb1—F6	84.78 (11)	Sb1—F6—Sb2	150.90 (15)
F3—Sb1—F6	87.33 (11)	C1—O2—C3	119.2 (3)
F1—Sb1—F6	85.11 (11)	O1—C1—O2	117.7 (4)
F9—Sb2—F11	95.48 (12)	O1—C1—C2	123.8 (4)
F9—Sb2—F8	90.04 (14)	O2—C1—C2	118.4 (4)
F11—Sb2—F8	94.12 (12)	C2 <sup>i</sup> —C2—C1	120.8 (5)
C3—O2—C1—O1	3.3 (5)	O1—C1—C2—C2 <sup>i</sup>	172.3 (5)
C3—O2—C1—C2	-176.4 (4)	O2—C1—C2—C2 <sup>i</sup>	-8.1 (7)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...F1	0.84	1.81	2.569 (4)	149
C3—H5...F9 <sup>ii</sup>	0.98	2.58	3.427 (5)	145

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C3—H3···F8	0.98	2.59	3.437 (5)	145
C2—H2···F10 <sup>iii</sup>	0.92 (4)	2.43 (4)	3.352 (5)	175 (3)

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Symmetry codes: (ii)  $-x+3/2, y+1/2, z$ ; (iii)  $x-1/2, -y+1/2, -z+1$ .