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# Synthesis and crystal structures of *N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate and *N*-isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate

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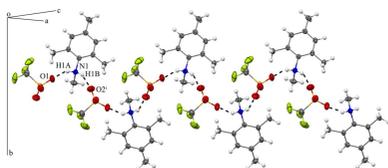
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Two 2,4,6-trimethylaniline-based trifluoromethanesulfonate (trifluoromethanesulfonate) salts were synthesized and characterized by single-crystal X-ray diffraction. *N*,2,4,6-Tetramethylanilinium trifluoromethanesulfonate, [C<sub>10</sub>H<sub>14</sub>NH<sub>2</sub><sup>+</sup>][CF<sub>3</sub>O<sub>3</sub>S<sup>-</sup>] (**1**), was synthesized *via* methylation of 2,4,6-trimethylaniline. *N*-Isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate, [C<sub>13</sub>H<sub>20</sub>N<sup>+</sup>][CF<sub>3</sub>O<sub>3</sub>S<sup>-</sup>] (**2**), was synthesized in a two-step reaction where the imine, *N*-isopropylidene-2,4,6-trimethylaniline, was first prepared *via* a dehydration reaction to form the Schiff base, followed by methylation using methyl trifluoromethanesulfonate to form the iminium ion. In compound **1**, both hydrogen bonding and  $\pi$ - $\pi$  interactions form the main intermolecular interactions. The primary interaction is a strong N—H $\cdots$ O hydrogen bond with the oxygen atoms of the trifluoromethanesulfonate anions bonded to the hydrogen atoms of the ammonium nitrogen atom to generate a one-dimensional chain. The [C<sub>10</sub>H<sub>14</sub>NH<sub>2</sub><sup>+</sup>] cations form dimers where the benzene rings form a  $\pi$ - $\pi$  interaction with a parallel-displaced geometry. The separation distance between the calculated centroids of the benzene rings is 3.9129 (8) Å, and the interplanar spacing and ring slippage between the dimers are 3.5156 (5) and 1.718 Å, respectively. For **2**, the [C<sub>13</sub>H<sub>20</sub>N<sup>+</sup>] cations also form dimers as in **1**, but with the benzene rings highly slipped. The distance between the calculated centroids of the benzene rings is 4.8937 (8) Å, and interplanar spacing and ring slippage are 3.3646 (5) and 3.553 Å, respectively. The major intermolecular interactions in **2** are instead a series of weaker C—H $\cdots$ O hydrogen bonds [C $\cdots$ O distances of 3.1723 (17), 3.3789 (18), and 3.3789 (18) Å], an interaction virtually absent in the structure of **1**. Fluorine atoms are not involved in strong directional interactions in either structure.

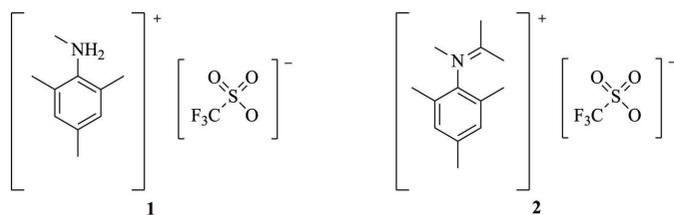
## 1. Chemical context

Aniline, the simplest aromatic amine, was first isolated by Otto Unverdorben in 1826 by the destruction of indigo dye. Since its discovery, aniline-based compounds have been extensively utilized as precursors to dyestuffs, pharmaceuticals, polymers, explosives, and industrial feedstocks (Travis, 2007). Of relevance to this work, *N*-methylaniline has been used to synthesize a variety of poly-*N*-methylaniline materials that function as electrodes, batteries, and nanocomposite sorbents to remove metal ions from solution (Lü *et al.*, 2014). In addition, *N*-substituted anilines, including *N*-methyl-2,4,6-trimethylaniline, have been used in the preparation of  $\alpha$ -amino diazoketones, which have been used as precursors in the synthesis of HIV inhibitors (Castoldi *et al.*, 2018).

Condensation of aniline with aldehydes and ketones leads to the formation of Schiff bases otherwise known as imines, of

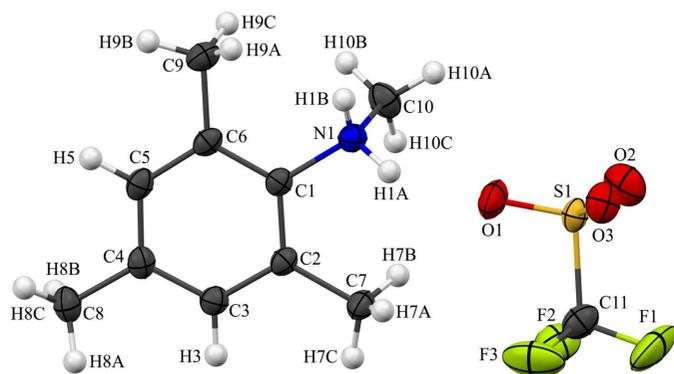


which the primary functional group is a carbon–nitrogen double bond (Tsuchimoto *et al.*, 1973; Layer, 1963). Addition of an extra atom or group to the imine nitrogen leads to the formation of iminium ions. Iminium ions have been identified as versatile intermediates in traditional organic chemistry, such as in the Knoevenagel and Mannich reactions and have also been utilized in the synthesis of natural products and pharmaceuticals (Erkkilä *et al.*, 2007; Böhme *et al.*, 1976). Herein, we report synthesis and characterization of two anilinium-based triflate salts, *N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate,  $[\text{C}_{10}\text{H}_{14}\text{NH}_2^+][\text{CF}_3\text{O}_3\text{S}^-]$  (**1**), and *N*-isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate,  $[\text{C}_{13}\text{H}_{20}\text{N}^+][\text{CF}_3\text{O}_3\text{S}^-]$  (**2**).



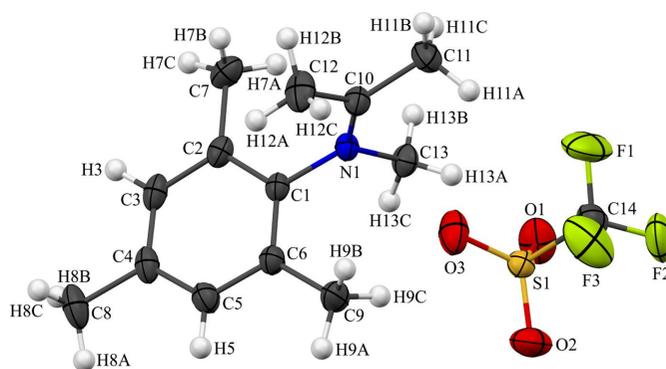
## 2. Structural commentary

Both compounds **1** and **2** are ionic compounds based on cations of a 2,4,6-trimethylanilinium unit with functionalization of the amine group and the anion trifluoromethanesulfonate (*i.e.* triflate). For **1**, a secondary ammonium ion results from bonds to a 2,4,6-trimethylphenyl ring, a methyl group, and two hydrogen atoms (Fig. 1). The hydrogen atoms of the ammonium nitrogen atom form hydrogen bonds with the oxygen atoms of neighboring triflate anions. For **2**, the iminium ion consists of an isopropylidene group (nitrogen atom double bonded to a carbon atom attached to two methyl groups) with a 2,4,6-trimethylphenyl ring and a methyl group also attached to the nitrogen (Fig. 2). As there are no hydrogen atoms on the iminium nitrogen atom, the organic cation of **2** does not form any classical hydrogen bonds. The



**Figure 1**

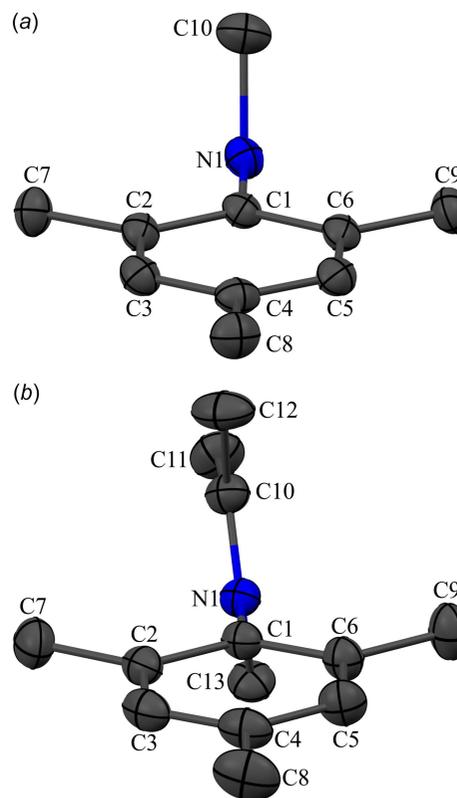
The single-crystal X-ray structure of *N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate,  $[\text{C}_{10}\text{H}_{14}\text{NH}_2^+][\text{CF}_3\text{O}_3\text{S}^-]$  (**1**). Displacement ellipsoids are at the 50% probability level. Color scheme: gray – carbon, blue – nitrogen, red – oxygen, yellow – fluorine, orange – sulfur, and white – hydrogen. All figures were generated with the program *Mercury* (Macrae *et al.*, 2020).



**Figure 2**

The single-crystal X-ray structure of *N*-methylisopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate,  $[\text{C}_{13}\text{H}_{20}\text{N}^+][\text{CF}_3\text{O}_3\text{S}^-]$  (**2**). See Fig. 1 for additional display details.

2,4,6-trimethylphenyl groups in both **1** and **2**, and the isopropylidene group in **2** are, as expected, nearly planar with r.m.s. deviations from planarity (including the nitrogen atom in the defined planes) of only 0.0263, 0.0111 and 0.0200 Å, respectively. In both compounds, the carbon functional groups of the nitrogen atom lie approximately perpendicular to the trimethylphenyl ring (Fig. 3). For **1**, the angle between the calculated mean plane of the methyl group (defined as C1, N1 and C10) and the mean plane of the aniline ring (N1 and C1–C6) is 89.71 (9)°, while for **2**, the angle between the mean



**Figure 3**

The organic functional groups bound to nitrogen atom are approximately orthogonal to the ring of the 2,4,6-trimethylphenyl group for both (a) **1** and (b) **2**. For clarity, the hydrogen atoms have been omitted. See Fig. 1 for additional display details.

**Table 1**

Angle Between the Mean Plane of the Organic Functional Groups and the Mean Plane of the Aniline Ring.

 Angles were determined with *SHELXL* (for **1** and **2**; Sheldrick, 2015b) or *Mercury* (for comparison compounds; Macrae *et al.*, 2020).

Compound	Angle (°)	CSD Reference Code	CCDC Deposition Number
<i>N</i> ,2,4,6-Tetramethylanilinium trifluoromethanesulfonate ( <b>1</b> )	89.71 (9)	This Work	
<i>N</i> -Isopropylidene- <i>N</i> ,2,4,6-tetramethylanilinium trifluoromethanesulfonate ( <b>2</b> )	85.15 (4)	This Work	
Dimesitylammonium pentafluorobenzenesulfonate	49.87 and 55.67	HIBFOO	297281
Dimesitylammonium tosylate	49.49 and 52.91	HIBGAB	604748
Oxonium <i>N</i> -(2,6-diphenylphenyl)mesitylammonium bis-(pentafluorobenzenesulfonate)	55.19	HIBFUU	297282
(2,4,6-Trimethylphenyl){2-[ <i>N</i> -(2,4,6-trimethylphenyl)formamido]ethyl}ammonium chloride	75.48	EDUWAD	878245
( <i>S</i> )-2-[[1-(Mesitylammonio)-3-methylbutan-2-yl]carbamoyl]benzenesulfonate	76.75	QARJUQ	843836
catena-[ <i>N</i> <sup>4</sup> , <i>N</i> <sup>4'</sup> ,3,3',5,5'-hexamethyl[1,1'-biphenyl]-4,4'-bis-(aminium) hexakis(μ-bromo)dilead(II)]	85.42	CATZEG	2145329
<i>N</i> -Methyl-1-[3-methyl-2-(2,4,6-trimethylphenyl)-2 <i>H</i> -indazol-7-yl]- <i>N</i> -(2,4,6-trimethylphenyl)ethan-1-iminium trifluoromethanesulfonate	82.92	JIFFAI	1842546
{2-[(Hydroxy)(methoxy)methylidene]-4-methoxy- <i>N</i> -methyl-4-oxo- <i>N</i> -(2,4,6-trimethylphenyl)butan-1-iminiumato}[tris-(pentafluorophenyl)]boron	80.47	RAVBIC	1504471

plane of the isopropylidene and methyl groups (C1, N1, and C10–C13) and the mean plane of the aniline ring (N1, C1–C6) is 85.15 (4)° (Table 1).

### 3. Supramolecular features

The dominant intermolecular forces in **1** consist of strong N–H···O hydrogen bonding (Table 2) and  $\pi$ – $\pi$  stacking interactions (Table 3), while in **2** no classical hydrogen bonds are present and  $\pi$ – $\pi$  interactions are highly slipped. Instead, interactions in **2** are governed by a series of weak C–H···O/F interactions (Table 4; listed H···O/F distances are up to 2.70 Å). Similar C–H···O interactions are also present in **1** but they are much less pronounced; the C–H···O distances and angles indicate that they are more likely dispersion (*i.e.* van der Waals) interactions rather than weak directional hydrogen bonds. For both compounds, C–H···F and C–H··· $\pi$  interactions are very weak and not well defined (Tables 2–4).

For **1**, the principal directional interactions are the N–H···O hydrogen bonds. Both ammonium hydrogen atoms are hydrogen bonded to an oxygen atom of neighboring triflate anions (Fig. 4; Table 2). One triflate anion is located on either side of the ammonium nitrogen atom. The hydrogen-bonding arrangement leads to a one-dimensional chain that

extends in the *ac* plane and is propagated by the *n*-glide plane at (*x*, 0.75, *z*). In addition, the organic cations form dimers with the 2,4,6-trimethylphenyl rings arranged in a parallel-displaced geometry where the 2,4,6-trimethylphenyl rings are offset relative to each other. The cations that make up the dimers are symmetry-related by inversion so that the ammonium groups are opposite of each other, likely to avoid Coulombic repulsions (Fig. 5). The distance between the calculated centroids of the benzene rings in each dimer is 3.9129 (8) Å, and the interplanar spacing and ring slippage are 3.5156 (5) and 1.718 Å, respectively [determined with *PLATON* (Spek, 2020); Table 3].

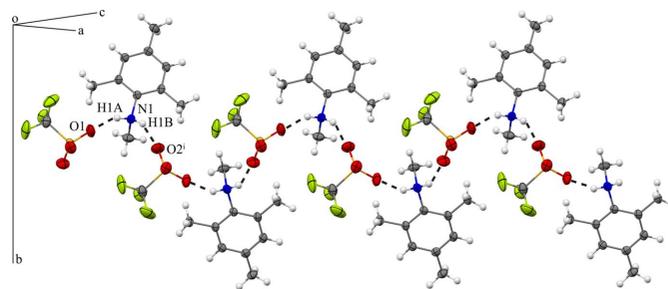
In **2**, the organic cations also form inversion-related dimers, but the rings are highly slipped (Fig. 5) with respect to each other and  $\pi$ – $\pi$  interaction, if present at all, is limited to just the outermost atoms C4 and C5. The distance between the calculated centroids of the benzene rings in each dimer is 4.8937 (8) Å, and interplanar spacing and ring slippage are 3.3646 (5) and 3.553 Å, respectively (Table 3). In the absence

**Table 2**

 Hydrogen-bond geometry (Å, °) for **1**.

<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>
N1–H1A···O1	0.91	1.92	2.7687 (16)	154
N1–H1B···O2 <sup>i</sup>	0.91	1.94	2.7669 (16)	150
C8–H8C···O1 <sup>ii</sup>	0.98	2.63	3.453 (2)	142
C8–H8C···O3 <sup>ii</sup>	0.98	2.69	3.6438 (19)	164
C8–H8A···O3 <sup>iii</sup>	0.98	2.55	3.504 (2)	165
C9–H9A···O2 <sup>i</sup>	0.98	2.63	3.333 (2)	129

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


**Figure 4**

Intermolecular hydrogen bonding in **1** between the ammonium hydrogen atoms and the trifluoromethanesulfonate oxygen atoms. The hydrogen bonding results in a one-dimensional chain that extends in the *ac* plane. For clarity, only the atoms involved in the hydrogen bonding are labeled. See Fig. 1 for additional display details. [Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ]

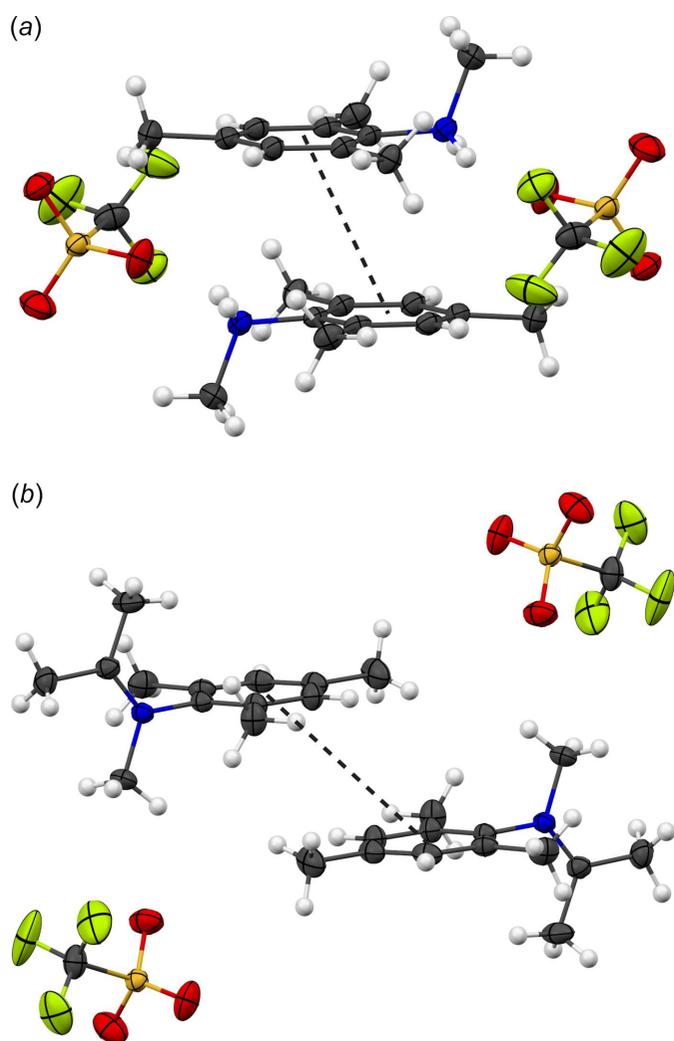
**Table 3**

$\pi$ - $\pi$  Interactions with parallel-displaced geometry (Å).

Distances determined with *PLATON* (Spek, 2020).

Compound/cation	Anion	Benzene ring centroid-centroid distance	Interplanar spacing	Slippage	CSD Refcode	CCDC Deposition Number
<i>N</i> ,2,4,6-Tetramethylanilinium	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	3.9129 (8)	3.5156 (5)	1.718	This Work (1)	
<i>N</i> -Isopropylidene- <i>N</i> ,2,4,6-tetramethylanilinium	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	4.8937 (8)	3.3646 (5)	3.553	This Work (2)	
1,3,5-Trimethylbenzene		4.6343 (9)	3.0727 (5)	2.850	SOPLAL01	618820 <sup>a</sup>
2,4,6-Trimethylanilinium	SO <sub>4</sub> <sup>2-</sup>	4.486 (2)	3.3028 (14)	2.434	AZUTOF	850619 <sup>b</sup>
2,4,6-Trimethylanilinium	SO <sub>4</sub> <sup>2-</sup>	4.489 (3)	3.2917 (16)	2.459	AZUTOF01	733935 <sup>c</sup>
2,4,6-Trimethylanilinium	Br <sup>-</sup>	5.362 (3)	3.3138 (18)	3.886	CUCTOK	750635 <sup>d</sup>
2,4,6-Trimethylanilinium	I <sup>-</sup>	5.5497 (14)	3.4087	4.379	JEVPUW	636623 <sup>e</sup>
2,4,6-Trimethylanilinium	Cl <sup>-</sup>	4.8109 (17)	3.4992 (9)	3.302	XIFQAF	654863 <sup>f</sup>
2,4,6-Trimethylanilinium	NO <sub>3</sub> <sup>-</sup>	5.3297 (17)	3.0222 (7)	3.928	YUKNUO	734678 <sup>g</sup>
2,4,6-Trimethylanilinium	ClO <sub>4</sub> <sup>-</sup>	5.374 (2)	3.6118 (8)	3.980	YUKPAW	734679 <sup>g</sup>
2,4,6-Trimethylanilinium	ClO <sub>4</sub> <sup>-</sup>	5.526 (11)	3.958 (10)	3.857	YUKPAW01	865148 <sup>h</sup>
2,4,6-Trimethylanilinium	ClO <sub>4</sub> <sup>-</sup>	5.340 (3)	3.6060 (17)	3.939	YUKPAW02	865149 <sup>h</sup>

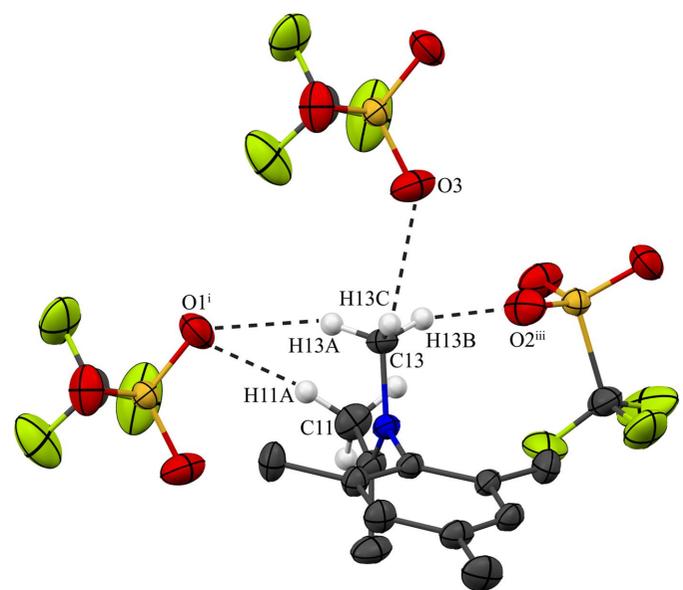
References: (a) Ibberson *et al.* (2007); (b) Rong (2011); (c) Kapoor *et al.* (2010a); (d) Cui & Xu (2009); (e) Lemmerer & Billing (2007); (f) Long *et al.* (2007); (g) Kapoor *et al.* (2010b); (h) Zhang *et al.* (2012).



**Figure 5**

The organic cations of (a) **1** and (b) **2** form dimers that are related by a crystallographic inversion center and have intermolecular  $\pi$ - $\pi$  interactions in a parallel-displaced geometry (black dotted lines). See Fig. 1 for additional display details.

of classical hydrogen bonding as well as significant  $\pi$ - $\pi$  interactions, other weak intermolecular forces become dominant in the structure of **2**. Most obvious are a series of weaker C—H...O interactions (Table 4). Most important are the hydrogen-bond-like interactions that involve the iminium methyl group (C13) being hydrogen bonded to oxygen atoms of three different triflate anions (Fig. 6). This methyl group is directly bonded to the nitrogen atom and carries the largest partial positive charge, inducing formation of charge-assisted bonds that are unusually short for C—H...O interactions with C...O distances of 3.1723 (17), 3.3789 (18), and 3.3789 (18) Å (Desiraju & Steiner, 2001). The isopropylidene methyl group



**Figure 6**

Intermolecular hydrogen bonding in **2** between the methyl hydrogen atoms of the [C<sub>13</sub>H<sub>20</sub>N<sup>+</sup>] cation and the oxygen atoms of three different trifluoromethanesulfonate anions. For clarity, only the hydrogen atoms on the methyl groups involved in the hydrogen bonding are shown and only the atoms involved in the hydrogen bonding are labeled. See Fig. 1 for additional display details. [Symmetry codes: (i)  $x + 1, y, z$ ; (iii)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ].

**Table 4**  
Hydrogen-bond geometry (Å, °) for **2**.

<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>
C11—H11A...O1 <sup>i</sup>	0.98	2.56	3.477 (2)	155
C12—H12A...F2 <sup>ii</sup>	0.98	2.69	3.3859 (18)	129
C13—H13A...O1 <sup>i</sup>	0.98	2.45	3.3789 (18)	159
C13—H13B...O2 <sup>iii</sup>	0.98	2.29	3.2377 (18)	162
C13—H13C...O3	0.98	2.52	3.1723 (17)	124

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

(C11) also does exhibit another unusually short C—H...O bond [C...O distance of 3.477 (2) Å] (Fig. 6). Each [C<sub>13</sub>H<sub>20</sub>N<sup>+</sup>] cation is hydrogen bonded to three triflate anions, and each triflate anion is hydrogen bonded to three organic cations, thereby generating a two-dimensional network of C—H...O interactions with layers extending perpendicular to the *b*-axis direction. The resulting layers interact with each other solely *via* dispersion interactions.

Both the centroid distance between the benzene rings and the ring slippage distance are longer for **2** than **1**. However, the values for **2** are more aligned with the distances for 1,3,5-trimethylbenzene, *i.e.* mesitylene. In the crystal structure of deuterated-1,3,5-trimethylbenzene (SOPLAL01; Ibberson *et al.*, 2007) the molecules also form long  $\pi$ – $\pi$  interactions with a parallel-displaced geometry, and the distance between the calculated centroids of neighboring benzene rings is 4.634 Å with a ring slippage of 2.850 Å (Table 3). Moreover, the longer distances of **2** are comparable to the centroid and ring slippage distances for a series of 2,4,6-trimethylanilinium cations with various counter-anions (Table 3).

#### 4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.45, update November 2023; Groom *et al.*, 2016) for secondary ammonium cations with a 2,4,6-trimethylphenyl group, as in **1**, yielded five entries (EDUWAD, HIBFOO, HIBFUU, HIBGAB and QARJUQ). Two of the cations have two 2,4,6-trimethylphenyl groups bound to the ammonium nitrogen atom but with different counter-anions, pentafluorobenzenesulfonate (HIBFOO; Sakakura *et al.*, 2007) or 4-methylbenzenesulfonate (HIBGAB; Sakakura *et al.*, 2007). A related secondary ammonium cation binds to one 2,4,6-trimethylphenyl group and one 2,6-diphenylphenyl group and the counter-anion is a pentafluorobenzenesulfonate (HIBFUU; Sakakura *et al.*, 2007). The last two entries also only contain one 2,4,6-trimethylphenyl group on the ammonium nitrogen atom. In one structure (EDUWAD; Ikhile & Bala, 2012), an ethyl-2-formamido-2,4,6-trimethylbenzene group is bound to the ammonium nitrogen atom and chloride serves as the counter-anion. The other structure (QARJUQ; Latham *et al.*, 2012) is a zwitterion with a 3-methylbutan-2-yl-carbamoylbenzenesulfonate acting as the second group bound to the ammonium nitrogen atom. Lastly, a biphenyl system with two secondary ammonium nitrogen atoms (CATZEG; Li *et al.*, 2022) is similar to **1**. As in **1**, the 1,1'-biphenyl system has an ammonium nitrogen attached to the carbon atom in the 4

and 4' positions of the benzene rings and on each benzene ring two methyl groups are located on carbon atoms adjacent (3,3' and 5,5' positions, respectively) to the carbon atom with the ammonium nitrogen atom. In addition, the ammonium nitrogen atoms bind to a methyl group as in **1**. A comparison of the angle between the mean planes of the functional groups and of the aniline ring reveal that the angles generally do not approach 90° as in **1** (Table 1; the angles were measured between mean planes defined in a similar manner as for **1** in the *Structural commentary* section). The angles range from *ca* 50 to 77° for the five structures with a 2,4,6-trimethylphenyl group attached to the ammonium nitrogen atom. For these structures, the bulkiness of the groups opposite the 2,4,6-trimethylphenyl groups may prevent the angle being close to 90°. In **1**, the group opposite to the 2,4,6-trimethylphenyl group is a smaller methyl group. For the 1,1'-biphenyl system (CATZEG) the angle (*ca* 85°) is closer to 90° likely due to the two phenyl rings nearly lying in the same plane and the presence of a smaller methyl group.

A survey for compounds containing an iminium nitrogen atom with a 2,4,6-trimethylphenyl ring and with a double-bonded carbon atom bound to two additional carbon groups yielded only one entry (JIFFAI; Kremláček *et al.*, 2018). Like **2**, the iminium nitrogen atom is bound to a methyl group and a 2,4,6-trimethylphenyl group and the counter-anion is triflate. Unlike **2**, substitution on the carbon atom of the iminium double bond consists of a methyl group and a bulky 3-methyl-2-(2,4,6-trimethylphenyl)-2*H*-indazol-7-yl group. Comparison of the equivalent angle between the mean planes of the functional groups and the aniline ring to that of **2** reveals that the angle (*ca* 83°) deviates more from 90° than that of **2** (Table 1). In a related structure (RAVBIC; Chen *et al.*, 2017), substitution on the carbon atom of the iminium double bond consists of a hydrogen atom and a {2-[(hydroxyl)(methoxy)methylidene]-4-methoxy-4-oxo}[[tris(pentafluorophenyl)]boron] group. In addition, the iminium nitrogen is bound to a methyl group. Also, this compound is a zwitterion instead of a triflate salt with the borate providing the negative charge. In regard to the angle between the mean planes of the functional groups and the aniline ring, there is an even larger deviation (*ca* 80°), likely due to the bulky {2-[(hydroxyl)(methoxy)methylidene]-4-methoxy-4-oxo}[[tris(pentafluorophenyl)]boron] group (Table 1).

#### 5. Synthesis and crystallization

##### Synthetic Materials

Methyl trifluoromethanesulfonate (98%) and 4 Å molecular sieves (8–12 mesh) were purchased from Sigma-Aldrich. Anhydrous diethyl ether (99%, ACS Grade) and 2,4,6-trimethylaniline (97%) were purchased from Thermo Scientific. Acetonitrile-*d*<sub>3</sub> (99 atom %D) was purchased from Acros Organics. Chloroform (99.5%) was purchased from Fisher Scientific. Acetone (99.5%) was purchased from VWR Chemicals. Chloroform was dried over 4 Å molecular sieves (8–12 mesh) prior to use. All other chemicals were used as received and without further purification.

**Table 5**  
Experimental details.

	1	2
Crystal data		
Chemical formula	[C <sub>10</sub> H <sub>16</sub> N <sup>+</sup> ][CF <sub>3</sub> O <sub>3</sub> S <sup>-</sup> ]	[C <sub>13</sub> H <sub>20</sub> N <sup>+</sup> ][CF <sub>3</sub> O <sub>3</sub> S <sup>-</sup> ]
<i>M<sub>r</sub></i>	299.31	339.37
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.5194 (7), 18.1257 (13), 9.0875 (8)	6.8580 (4), 19.4619 (12), 12.6131 (7)
$\beta$ (°)	105.106 (3)	102.024 (2)
<i>V</i> (Å <sup>3</sup> )	1354.80 (19)	1646.53 (17)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.28	0.24
Crystal size (mm)	0.45 × 0.43 × 0.21	0.45 × 0.43 × 0.32
Data collection		
Diffractometer	Bruker AXS D8 Quest	Bruker AXS D8 Quest
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.559, 0.747	0.662, 0.747
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	47829, 5186, 3572	35093, 6151, 4836
<i>R</i> <sub>int</sub>	0.093	0.040
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.772	0.770
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.047, 0.133, 1.03	0.045, 0.136, 1.04
No. of reflections	5186	6151
No. of parameters	176	205
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.42, -0.56	0.63, -0.41

Computer programs: *APEX4* and *SAINT* (Bruker, 2022), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *ShelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2020), and *pubCIF* (Westrip, 2010).

***N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate (1)** (29.2%). Dried chloroform (2.0 mL), methyl trifluoromethanesulfonate (0.290 mL, 2.4 mmol, 1.1 eq) and a stir bar were added to a dry 10 mL round-bottom flask flushed with nitrogen gas. 2,4,5-trimethylaniline (0.3200 g, 2.4 mmol, 1 eq) was dissolved in 1.0 mL of dried chloroform and added dropwise to the flask with stirring over ice with the resulting solution appearing clear and colorless. The flask was allowed to stir for 15 min over ice and an additional 30 min at room temperature. House vacuum was then used to remove the solvent, leaving behind an off-white powder. The powder was redissolved in 1–2 mL of dried chloroform with 10 drops of anhydrous diethyl ether. Clear, colorless crystals were grown in 1–2 days by slow evaporation of the solvent at room temperature. The clear crystals (0.2090 g, 29.2%) were vacuum filtered and washed with 5.0 mL of anhydrous diethyl ether. A portion of the crystals were separated for X-ray diffraction analysis with the remaining sample being analyzed as follows: m.p. 429.2–430.5 K; IR (ATR)  $\nu_{\max}$  3082 cm<sup>-1</sup> (N<sup>+</sup>–H stretch), 1610 cm<sup>-1</sup> (N<sup>+</sup>–H bend); <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 80 MHz):  $\delta$  2.29 (s, 3 H), 2.40 (s, 6 H), 3.02 (t, *J* = 2.83 Hz, 3 H), 7.04 (s, 1 H); <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 80 MHz):  $\delta$  17.24, 20.68, 37.43, 131.50, 131.76, 132.18, 140.84.

***N*-isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate (2)** (20.7% over two steps). Synthesis was carried out using a two-step process. In step one, *N*-isopropylidene-2,4,6-trimethylaniline was synthesized utilizing the procedure published by Tsuchimoto *et al.* (1973). Anhydrous diethyl ether (35.1 mL) was added to a 60 mL amber glass bottle followed by 2,4,6-trimethylaniline (1.5241 g,

11.3 mmol, 1 eq), acetone (1.00 mL, 13.6 mmol, 1.2 eq), and 4 Å molecular sieves (15.6 g) resulting in a clear, slightly brown solution. The bottle was moved to the fridge and reaction progress was monitored by observing the disappearance of the 2,4,6-trimethylaniline peaks by <sup>1</sup>H-NMR. After about 4 days, the sieves were removed by gravity filtration and washed with three 10 mL portions of anhydrous diethyl ether. The resulting solution was rotary evaporated yielding a clear, colorless oil (1.4867 g, 75.3%). The oil was purified by fractional short path vacuum distillation (338.8–340.3 K at 1 mm Hg) to yield three clear liquid fractions, with the second fraction (0.4686 g, 23.7% post-distillation) being used in the next step. IR (ATR)  $\nu_{\max}$  1670 cm<sup>-1</sup> (C=N stretch); <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 80 MHz):  $\delta$  1.58 (s, 3 H), 1.90 (s, 6 H), 2.15 (s, 3 H), 2.21 (s, 3 H), 6.82 (s, 2 H); <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 80 MHz):  $\delta$  17.98, 20.86, 27.73, 126.61, 129.33, 132.33, 147.69, 169.49.

In step two, dried chloroform (2.0 mL), methyl trifluoromethanesulfonate (0.324 mL, 2.9 mmol, 1.1 eq) and a stir bar were added to a dry 10 mL round-bottom flask flushed with nitrogen. *N*-isopropylidene-2,4,6-trimethylaniline (0.4686 g, 2.7 mmol, 1 eq) was dissolved in dried chloroform (1 mL) and added dropwise to the flask with stirring over ice resulting a clear and colorless solution. The flask was allowed to stir for 15 min over ice and an additional 30 min at room temperature. Upon completion, house vacuum was used to remove the solvent, leaving behind an off-white powder. The powder was then redissolved in 1–2 mL of dried chloroform with 10 drops of anhydrous diethyl ether. White crystals were grown in 1–2 days by slow evaporation of the solvent at room temperature.

The white crystals (0.7931 g, 87.4%) were vacuum filtered and washed with 5.0 mL of anhydrous diethyl ether. A portion of the crystals were separated for X-ray diffraction analysis with the remaining sample being analyzed as follows: m.p. 359.0–360.4 K; IR (ATR)  $\nu_{\max}$  1648  $\text{cm}^{-1}$  (C=N stretch);  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 80 MHz):  $\delta$  2.16 (s, 6 H), 2.25 (s, 3 H), 2.33 (s, 3 H), 2.74 (s, 3 H), 3.77 (s, 3 H), 7.12 (s, 2 H);  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CD}_3\text{CN}$ , 80 MHz):  $\delta$  16.98, 20.81, 24.93, 26.09, 45.42, 131.01, 131.90, 141.50, 196.51.

### Physical Methods

The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were reported in ppm ( $\delta$ ) and referenced to  $\text{CD}_3\text{CN}$ . All NMR spectra were recorded at 299.7 K on a Magritek Spinsolve 80 (Malvern, PA USA). Proton and carbon spectra were operated at 80.98 MHz and 20.36 MHz, respectively, with a field strength of 1.88 Tesla. Spectra were processed using MNova software Ver. 14.3.3 (Mestrelab Research, Escondido, CA USA). Infrared spectroscopy was performed using a Nicolet iS5 FTIR spectrometer (Thermo Electron North America LLC) outfitted with a diamond crystal ATR accessory and Omnic software Omnic version 9.2.98.

### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. Hydrogen atoms were placed in calculated positions and refined as riding on their carrier atoms with C–H distances of 0.95 Å for  $sp^2$  carbon atoms, 0.98 Å for methyl carbon atoms, and 0.91 Å for ammonium nitrogen atoms. Methyl hydrogen atoms were allowed to rotate but not to tip to best fit the experimental electron density. The  $U_{\text{iso}}$  values for hydrogen atoms were set to a multiple of the value of the carrying carbon atom or nitrogen atom (1.2 times for  $sp^2$ -hybridized carbon atoms and the nitrogen atom or 1.5 times for methyl carbon atoms).

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## supporting information

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## Synthesis and crystal structures of *N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate and *N*-isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate

John W. Stewart, Elena M. Irons, Giovanna Osorio Abanto, Matthias Zeller, Curtis M. Zaleski and Daniel P. Predecki

### Computing details

#### *N*,2,4,6-Tetramethylanilinium trifluoromethanesulfonate (1)

##### Crystal data

$C_{10}H_{16}N^+ \cdot CF_3O_3S^-$

$M_r = 299.31$

Monoclinic,  $P2_1/n$

$a = 8.5194$  (7) Å

$b = 18.1257$  (13) Å

$c = 9.0875$  (8) Å

$\beta = 105.106$  (3)°

$V = 1354.80$  (19) Å<sup>3</sup>

$Z = 4$

$F(000) = 624$

$D_x = 1.467$  Mg m<sup>-3</sup>

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

Cell parameters from 9989 reflections

$\theta = 2.6$ – $32.7$ °

$\mu = 0.28$  mm<sup>-1</sup>

$T = 150$  K

Plate, colourless

$0.45 \times 0.43 \times 0.21$  mm

##### Data collection

Bruker AXS D8 Quest  
diffractometer

Radiation source: fine focus sealed tube X-ray  
source

Triumph curved graphite crystal  
monochromator

Detector resolution: 7.4074 pixels mm<sup>-1</sup>

$\omega$  and  $\phi$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.559$ ,  $T_{\max} = 0.747$

47829 measured reflections

5186 independent reflections

3572 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.093$

$\theta_{\max} = 33.3$ °,  $\theta_{\min} = 2.6$ °

$h = -13$ → $12$

$k = -27$ → $27$

$l = -13$ → $14$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.133$

$S = 1.03$

5186 reflections

176 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 0.3108P]$

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

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

$\Delta\rho_{\max} = 0.42$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>

*Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.26254 (4)	0.70859 (2)	0.03063 (4)	0.02587 (10)
F1	0.06186 (16)	0.66503 (9)	−0.22410 (12)	0.0730 (4)
F2	−0.00260 (12)	0.62874 (6)	−0.02375 (13)	0.0491 (3)
F3	0.19455 (15)	0.57716 (7)	−0.08796 (18)	0.0703 (4)
O1	0.31540 (15)	0.67224 (7)	0.17559 (12)	0.0431 (3)
O2	0.16299 (15)	0.77239 (7)	0.03049 (17)	0.0469 (3)
O3	0.38537 (14)	0.71728 (7)	−0.04960 (13)	0.0380 (3)
N1	0.38672 (14)	0.64116 (6)	0.48425 (12)	0.0243 (2)
H1A	0.358888	0.636006	0.381079	0.029*
H1B	0.493405	0.654345	0.513906	0.029*
C1	0.36660 (15)	0.56949 (7)	0.55382 (14)	0.0221 (2)
C2	0.24275 (15)	0.52245 (7)	0.47553 (14)	0.0229 (2)
C3	0.21912 (17)	0.45701 (7)	0.54737 (15)	0.0252 (2)
H3	0.136131	0.424047	0.496070	0.030*
C4	0.31396 (16)	0.43847 (7)	0.69272 (15)	0.0252 (3)
C5	0.43919 (16)	0.48619 (8)	0.76333 (14)	0.0257 (3)
H5	0.507495	0.473066	0.860156	0.031*
C6	0.46785 (15)	0.55238 (7)	0.69717 (14)	0.0236 (2)
C7	0.13840 (17)	0.53992 (8)	0.31822 (15)	0.0282 (3)
H7A	0.204815	0.537779	0.245017	0.042*
H7B	0.092515	0.589532	0.317709	0.042*
H7C	0.050034	0.503828	0.289669	0.042*
C8	0.27871 (19)	0.37021 (8)	0.77291 (17)	0.0318 (3)
H8A	0.219874	0.334557	0.697413	0.048*
H8B	0.212107	0.383332	0.842138	0.048*
H8C	0.381199	0.348317	0.831371	0.048*
C9	0.60280 (17)	0.60290 (8)	0.77978 (16)	0.0305 (3)
H9A	0.673863	0.614143	0.713537	0.046*
H9B	0.666105	0.578630	0.872717	0.046*
H9C	0.556113	0.648773	0.806764	0.046*
C10	0.2861 (2)	0.70206 (8)	0.52615 (18)	0.0338 (3)
H10A	0.304250	0.747882	0.475748	0.051*
H10B	0.317801	0.709186	0.636870	0.051*
H10C	0.170738	0.688743	0.493086	0.051*
C11	0.1221 (2)	0.64161 (10)	−0.08269 (18)	0.0374 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.02667 (16)	0.03106 (18)	0.02113 (15)	0.00514 (13)	0.00846 (11)	0.00329 (12)
F1	0.0665 (8)	0.1198 (12)	0.0243 (5)	-0.0232 (8)	-0.0031 (5)	0.0009 (6)
F2	0.0354 (5)	0.0635 (7)	0.0509 (6)	-0.0111 (5)	0.0155 (4)	-0.0054 (5)
F3	0.0570 (7)	0.0532 (7)	0.1026 (11)	-0.0022 (6)	0.0240 (7)	-0.0397 (7)
O1	0.0452 (6)	0.0557 (7)	0.0246 (5)	-0.0077 (6)	0.0022 (4)	0.0128 (5)
O2	0.0396 (6)	0.0398 (6)	0.0647 (9)	0.0121 (5)	0.0197 (6)	-0.0029 (6)
O3	0.0346 (5)	0.0491 (7)	0.0350 (6)	0.0031 (5)	0.0174 (5)	0.0045 (5)
N1	0.0262 (5)	0.0269 (5)	0.0212 (5)	-0.0026 (4)	0.0084 (4)	-0.0013 (4)
C1	0.0247 (5)	0.0245 (6)	0.0192 (5)	0.0002 (5)	0.0095 (4)	-0.0013 (4)
C2	0.0228 (5)	0.0280 (6)	0.0187 (5)	0.0001 (5)	0.0072 (4)	-0.0007 (4)
C3	0.0277 (6)	0.0268 (6)	0.0226 (5)	-0.0015 (5)	0.0092 (5)	-0.0013 (5)
C4	0.0294 (6)	0.0258 (6)	0.0231 (6)	0.0043 (5)	0.0118 (5)	0.0014 (5)
C5	0.0275 (6)	0.0315 (7)	0.0190 (5)	0.0041 (5)	0.0079 (4)	-0.0001 (5)
C6	0.0236 (5)	0.0300 (6)	0.0185 (5)	0.0014 (5)	0.0076 (4)	-0.0037 (4)
C7	0.0278 (6)	0.0336 (7)	0.0217 (6)	-0.0034 (5)	0.0037 (5)	0.0027 (5)
C8	0.0378 (7)	0.0307 (7)	0.0290 (7)	0.0030 (6)	0.0124 (6)	0.0069 (5)
C9	0.0302 (7)	0.0364 (7)	0.0237 (6)	-0.0027 (6)	0.0049 (5)	-0.0046 (5)
C10	0.0411 (8)	0.0264 (7)	0.0382 (8)	0.0043 (6)	0.0176 (6)	0.0005 (6)
C11	0.0352 (7)	0.0486 (9)	0.0288 (7)	0.0009 (7)	0.0088 (6)	-0.0056 (6)

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

S1—O3	1.4315 (11)	C4—C5	1.393 (2)
S1—O2	1.4339 (12)	C4—C8	1.5052 (19)
S1—O1	1.4364 (11)	C5—C6	1.3918 (19)
S1—C11	1.8230 (17)	C5—H5	0.9500
F1—C11	1.3234 (19)	C6—C9	1.5080 (19)
F2—C11	1.3293 (19)	C7—H7A	0.9800
F3—C11	1.328 (2)	C7—H7B	0.9800
N1—C1	1.4742 (17)	C7—H7C	0.9800
N1—C10	1.5062 (18)	C8—H8A	0.9800
N1—H1A	0.9100	C8—H8B	0.9800
N1—H1B	0.9100	C8—H8C	0.9800
C1—C6	1.3970 (18)	C9—H9A	0.9800
C1—C2	1.3983 (18)	C9—H9B	0.9800
C2—C3	1.3935 (18)	C9—H9C	0.9800
C2—C7	1.5073 (18)	C10—H10A	0.9800
C3—C4	1.3980 (18)	C10—H10B	0.9800
C3—H3	0.9500	C10—H10C	0.9800
O3—S1—O2	114.93 (8)	C2—C7—H7A	109.5
O3—S1—O1	114.93 (7)	C2—C7—H7B	109.5
O2—S1—O1	114.51 (8)	H7A—C7—H7B	109.5
O3—S1—C11	104.16 (7)	C2—C7—H7C	109.5
O2—S1—C11	103.63 (8)	H7A—C7—H7C	109.5

O1—S1—C11	102.43 (7)	H7B—C7—H7C	109.5
C1—N1—C10	113.57 (10)	C4—C8—H8A	109.5
C1—N1—H1A	108.9	C4—C8—H8B	109.5
C10—N1—H1A	108.9	H8A—C8—H8B	109.5
C1—N1—H1B	108.9	C4—C8—H8C	109.5
C10—N1—H1B	108.9	H8A—C8—H8C	109.5
H1A—N1—H1B	107.7	H8B—C8—H8C	109.5
C6—C1—C2	122.66 (12)	C6—C9—H9A	109.5
C6—C1—N1	118.88 (11)	C6—C9—H9B	109.5
C2—C1—N1	118.41 (11)	H9A—C9—H9B	109.5
C3—C2—C1	117.56 (12)	C6—C9—H9C	109.5
C3—C2—C7	120.11 (12)	H9A—C9—H9C	109.5
C1—C2—C7	122.32 (12)	H9B—C9—H9C	109.5
C2—C3—C4	121.93 (12)	N1—C10—H10A	109.5
C2—C3—H3	119.0	N1—C10—H10B	109.5
C4—C3—H3	119.0	H10A—C10—H10B	109.5
C5—C4—C3	118.07 (12)	N1—C10—H10C	109.5
C5—C4—C8	120.84 (12)	H10A—C10—H10C	109.5
C3—C4—C8	121.06 (13)	H10B—C10—H10C	109.5
C6—C5—C4	122.39 (12)	F1—C11—F3	108.27 (15)
C6—C5—H5	118.8	F1—C11—F2	107.40 (14)
C4—C5—H5	118.8	F3—C11—F2	106.73 (15)
C5—C6—C1	117.33 (12)	F1—C11—S1	111.49 (13)
C5—C6—C9	120.35 (12)	F3—C11—S1	111.33 (12)
C1—C6—C9	122.33 (12)	F2—C11—S1	111.41 (11)
C10—N1—C1—C6	-89.12 (15)	C2—C1—C6—C5	-1.40 (18)
C10—N1—C1—C2	88.69 (14)	N1—C1—C6—C5	176.31 (11)
C6—C1—C2—C3	1.63 (19)	C2—C1—C6—C9	179.04 (12)
N1—C1—C2—C3	-176.09 (11)	N1—C1—C6—C9	-3.25 (18)
C6—C1—C2—C7	-177.50 (12)	O3—S1—C11—F1	-58.65 (14)
N1—C1—C2—C7	4.78 (18)	O2—S1—C11—F1	61.92 (14)
C1—C2—C3—C4	0.40 (19)	O1—S1—C11—F1	-178.71 (12)
C7—C2—C3—C4	179.54 (12)	O3—S1—C11—F3	62.38 (14)
C2—C3—C4—C5	-2.52 (19)	O2—S1—C11—F3	-177.05 (13)
C2—C3—C4—C8	175.57 (12)	O1—S1—C11—F3	-57.68 (14)
C3—C4—C5—C6	2.77 (19)	O3—S1—C11—F2	-178.61 (11)
C8—C4—C5—C6	-175.32 (12)	O2—S1—C11—F2	-58.04 (14)
C4—C5—C6—C1	-0.87 (19)	O1—S1—C11—F2	61.33 (13)
C4—C5—C6—C9	178.69 (12)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O1	0.91	1.92	2.7687 (16)	154
N1—H1B $\cdots$ O2 <sup>i</sup>	0.91	1.94	2.7669 (16)	150
C8—H8C $\cdots$ O1 <sup>ii</sup>	0.98	2.63	3.453 (2)	142
C8—H8C $\cdots$ O3 <sup>ii</sup>	0.98	2.69	3.6438 (19)	164

C8—H8A···O3 <sup>iii</sup>	0.98	2.55	3.504 (2)	165
C9—H9A···O2 <sup>i</sup>	0.98	2.63	3.333 (2)	129

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

### *N*-Isopropylidene-*N*,2,4,6-tetramethylanilinium trifluoromethanesulfonate (2)

#### Crystal data

$C_{13}H_{20}N^+ \cdot CF_3O_3S^-$	$F(000) = 712$
$M_r = 339.37$	$D_x = 1.369 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.8580 (4) \text{ \AA}$	Cell parameters from 9901 reflections
$b = 19.4619 (12) \text{ \AA}$	$\theta = 2.7\text{--}33.1^\circ$
$c = 12.6131 (7) \text{ \AA}$	$\mu = 0.24 \text{ mm}^{-1}$
$\beta = 102.024 (2)^\circ$	$T = 150 \text{ K}$
$V = 1646.53 (17) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.45 \times 0.43 \times 0.32 \text{ mm}$

#### Data collection

Bruker AXS D8 Quest diffractometer	$T_{\min} = 0.662, T_{\max} = 0.747$
Radiation source: fine focus sealed tube X-ray source	35093 measured reflections
Triumph curved graphite crystal monochromator	6151 independent reflections
Detector resolution: $7.4074 \text{ pixels mm}^{-1}$	4836 reflections with $I > 2\sigma(I)$
$\omega$ and phi scans	$R_{\text{int}} = 0.040$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\max} = 33.2^\circ, \theta_{\min} = 2.0^\circ$
	$h = -10 \rightarrow 10$
	$k = -29 \rightarrow 28$
	$l = -19 \rightarrow 19$

#### Refinement

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.6525P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\max} = 0.036$
6151 reflections	$\Delta\rho_{\max} = 0.63 \text{ e \AA}^{-3}$
205 parameters	$\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
0 restraints	

#### Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.15479 (4)	0.79780 (2)	0.61391 (2)	0.02550 (8)
F1	0.3761 (3)	0.86287 (8)	0.77561 (9)	0.0851 (5)
F2	0.2530 (2)	0.92744 (5)	0.64188 (11)	0.0664 (3)
F3	0.49502 (18)	0.86146 (8)	0.63158 (12)	0.0734 (4)
O1	-0.02107 (18)	0.81355 (7)	0.65353 (12)	0.0494 (3)

O2	0.1341 (2)	0.80438 (7)	0.49895 (9)	0.0507 (3)
O3	0.25615 (18)	0.73657 (6)	0.66054 (11)	0.0496 (3)
N1	0.86535 (15)	0.64144 (5)	0.77099 (8)	0.02325 (18)
C1	0.81204 (17)	0.57568 (6)	0.71732 (9)	0.0235 (2)
C2	0.73919 (18)	0.52358 (6)	0.77498 (10)	0.0266 (2)
C3	0.68216 (19)	0.46217 (6)	0.72058 (12)	0.0310 (3)
H3	0.631492	0.426053	0.757740	0.037*
C4	0.69727 (19)	0.45226 (7)	0.61361 (12)	0.0318 (3)
C5	0.7696 (2)	0.50569 (7)	0.55946 (11)	0.0320 (3)
H5	0.779749	0.499239	0.486153	0.038*
C6	0.82752 (19)	0.56836 (6)	0.60949 (10)	0.0269 (2)
C7	0.7275 (2)	0.53217 (8)	0.89215 (12)	0.0370 (3)
H7A	0.675490	0.577958	0.903002	0.055*
H7B	0.860854	0.526986	0.937972	0.055*
H7C	0.638530	0.497155	0.911733	0.055*
C8	0.6377 (2)	0.38445 (8)	0.55818 (16)	0.0450 (4)
H8A	0.613907	0.390669	0.479424	0.067*
H8B	0.515577	0.367745	0.578344	0.067*
H8C	0.744876	0.350912	0.580769	0.067*
C9	0.9047 (2)	0.62569 (7)	0.54963 (12)	0.0365 (3)
H9A	0.898812	0.611766	0.474357	0.055*
H9B	1.043117	0.635892	0.584635	0.055*
H9C	0.822601	0.666766	0.550892	0.055*
C10	1.03905 (18)	0.65257 (6)	0.83181 (10)	0.0274 (2)
C11	1.0819 (2)	0.71841 (7)	0.89199 (12)	0.0368 (3)
H11A	1.071297	0.756521	0.840322	0.055*
H11B	1.217001	0.717058	0.936743	0.055*
H11C	0.985468	0.725038	0.938559	0.055*
C12	1.2004 (2)	0.60056 (8)	0.84344 (15)	0.0411 (3)
H12A	1.148345	0.558503	0.805015	0.062*
H12B	1.249569	0.590234	0.920420	0.062*
H12C	1.309884	0.618616	0.812571	0.062*
C13	0.70636 (19)	0.69461 (6)	0.75334 (11)	0.0293 (2)
H13A	0.758175	0.737207	0.728243	0.044*
H13B	0.663458	0.703278	0.821535	0.044*
H13C	0.592598	0.678426	0.698583	0.044*
C14	0.3300 (3)	0.86552 (8)	0.66949 (12)	0.0387 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.02328 (14)	0.02674 (14)	0.02618 (14)	-0.00154 (10)	0.00446 (10)	-0.00088 (10)
F1	0.1245 (13)	0.0883 (10)	0.0321 (5)	-0.0545 (9)	-0.0077 (6)	-0.0097 (6)
F2	0.0969 (10)	0.0280 (5)	0.0795 (8)	-0.0120 (5)	0.0304 (7)	-0.0050 (5)
F3	0.0431 (6)	0.0875 (9)	0.0941 (10)	-0.0345 (6)	0.0248 (6)	-0.0337 (8)
O1	0.0396 (6)	0.0469 (6)	0.0695 (8)	-0.0009 (5)	0.0291 (6)	-0.0024 (6)
O2	0.0612 (8)	0.0616 (8)	0.0282 (5)	-0.0198 (6)	0.0068 (5)	-0.0046 (5)
O3	0.0405 (6)	0.0309 (5)	0.0708 (8)	0.0043 (4)	-0.0036 (6)	0.0016 (5)

N1	0.0232 (4)	0.0196 (4)	0.0266 (4)	0.0017 (3)	0.0043 (3)	0.0010 (3)
C1	0.0221 (5)	0.0191 (4)	0.0286 (5)	-0.0006 (4)	0.0036 (4)	0.0011 (4)
C2	0.0235 (5)	0.0235 (5)	0.0324 (5)	0.0009 (4)	0.0050 (4)	0.0063 (4)
C3	0.0259 (6)	0.0206 (5)	0.0461 (7)	-0.0013 (4)	0.0063 (5)	0.0071 (5)
C4	0.0265 (6)	0.0204 (5)	0.0466 (7)	-0.0025 (4)	0.0032 (5)	-0.0026 (5)
C5	0.0351 (6)	0.0269 (6)	0.0335 (6)	-0.0043 (5)	0.0062 (5)	-0.0046 (5)
C6	0.0293 (6)	0.0228 (5)	0.0288 (5)	-0.0032 (4)	0.0069 (4)	0.0002 (4)
C7	0.0401 (7)	0.0387 (7)	0.0335 (6)	0.0011 (6)	0.0110 (5)	0.0099 (5)
C8	0.0404 (8)	0.0247 (6)	0.0681 (11)	-0.0077 (5)	0.0073 (7)	-0.0115 (6)
C9	0.0496 (8)	0.0298 (6)	0.0328 (6)	-0.0107 (6)	0.0145 (6)	0.0006 (5)
C10	0.0257 (5)	0.0237 (5)	0.0310 (5)	-0.0004 (4)	0.0022 (4)	0.0016 (4)
C11	0.0405 (7)	0.0300 (6)	0.0367 (6)	-0.0056 (5)	0.0004 (5)	-0.0065 (5)
C12	0.0256 (6)	0.0317 (7)	0.0604 (9)	0.0039 (5)	-0.0042 (6)	0.0033 (6)
C13	0.0266 (6)	0.0253 (5)	0.0360 (6)	0.0076 (4)	0.0066 (5)	0.0024 (4)
C14	0.0479 (8)	0.0345 (7)	0.0344 (6)	-0.0132 (6)	0.0101 (6)	-0.0067 (5)

*Geometric parameters (Å, °)*

S1—O1	1.4315 (12)	C7—H7A	0.9800
S1—O2	1.4330 (12)	C7—H7B	0.9800
S1—O3	1.4419 (12)	C7—H7C	0.9800
S1—C14	1.8226 (15)	C8—H8A	0.9800
F1—C14	1.3107 (18)	C8—H8B	0.9800
F2—C14	1.333 (2)	C8—H8C	0.9800
F3—C14	1.319 (2)	C9—H9A	0.9800
N1—C10	1.2937 (16)	C9—H9B	0.9800
N1—C1	1.4584 (15)	C9—H9C	0.9800
N1—C13	1.4860 (15)	C10—C12	1.4843 (18)
C1—C6	1.3934 (17)	C10—C11	1.4871 (18)
C1—C2	1.3994 (16)	C11—H11A	0.9800
C2—C3	1.3929 (18)	C11—H11B	0.9800
C2—C7	1.5060 (19)	C11—H11C	0.9800
C3—C4	1.388 (2)	C12—H12A	0.9800
C3—H3	0.9500	C12—H12B	0.9800
C4—C5	1.3910 (19)	C12—H12C	0.9800
C4—C8	1.5095 (19)	C13—H13A	0.9800
C5—C6	1.3925 (17)	C13—H13B	0.9800
C5—H5	0.9500	C13—H13C	0.9800
C6—C9	1.5039 (18)		
O1—S1—O2	114.90 (9)	C4—C8—H8C	109.5
O1—S1—O3	113.84 (8)	H8A—C8—H8C	109.5
O2—S1—O3	115.11 (8)	H8B—C8—H8C	109.5
O1—S1—C14	104.29 (8)	C6—C9—H9A	109.5
O2—S1—C14	104.07 (7)	C6—C9—H9B	109.5
O3—S1—C14	102.57 (8)	H9A—C9—H9B	109.5
C10—N1—C1	122.21 (10)	C6—C9—H9C	109.5
C10—N1—C13	121.91 (11)	H9A—C9—H9C	109.5

C1—N1—C13	115.87 (10)	H9B—C9—H9C	109.5
C6—C1—C2	122.77 (11)	N1—C10—C12	121.33 (12)
C6—C1—N1	118.69 (10)	N1—C10—C11	120.42 (12)
C2—C1—N1	118.47 (11)	C12—C10—C11	118.25 (12)
C3—C2—C1	117.36 (12)	C10—C11—H11A	109.5
C3—C2—C7	120.79 (12)	C10—C11—H11B	109.5
C1—C2—C7	121.83 (12)	H11A—C11—H11B	109.5
C4—C3—C2	121.87 (12)	C10—C11—H11C	109.5
C4—C3—H3	119.1	H11A—C11—H11C	109.5
C2—C3—H3	119.1	H11B—C11—H11C	109.5
C3—C4—C5	118.67 (12)	C10—C12—H12A	109.5
C3—C4—C8	120.26 (13)	C10—C12—H12B	109.5
C5—C4—C8	121.06 (14)	H12A—C12—H12B	109.5
C4—C5—C6	121.98 (12)	C10—C12—H12C	109.5
C4—C5—H5	119.0	H12A—C12—H12C	109.5
C6—C5—H5	119.0	H12B—C12—H12C	109.5
C5—C6—C1	117.34 (11)	N1—C13—H13A	109.5
C5—C6—C9	121.29 (12)	N1—C13—H13B	109.5
C1—C6—C9	121.37 (11)	H13A—C13—H13B	109.5
C2—C7—H7A	109.5	N1—C13—H13C	109.5
C2—C7—H7B	109.5	H13A—C13—H13C	109.5
H7A—C7—H7B	109.5	H13B—C13—H13C	109.5
C2—C7—H7C	109.5	F1—C14—F3	108.99 (16)
H7A—C7—H7C	109.5	F1—C14—F2	107.49 (14)
H7B—C7—H7C	109.5	F3—C14—F2	106.43 (14)
C4—C8—H8A	109.5	F1—C14—S1	111.32 (11)
C4—C8—H8B	109.5	F3—C14—S1	111.33 (11)
H8A—C8—H8B	109.5	F2—C14—S1	111.08 (12)
C10—N1—C1—C6	-97.12 (14)	N1—C1—C6—C5	-178.02 (11)
C13—N1—C1—C6	84.04 (14)	C2—C1—C6—C9	179.42 (13)
C10—N1—C1—C2	85.64 (15)	N1—C1—C6—C9	2.30 (18)
C13—N1—C1—C2	-93.20 (13)	C1—N1—C10—C12	4.98 (19)
C6—C1—C2—C3	0.47 (18)	C13—N1—C10—C12	-176.25 (13)
N1—C1—C2—C3	177.60 (10)	C1—N1—C10—C11	-175.12 (12)
C6—C1—C2—C7	178.81 (12)	C13—N1—C10—C11	3.65 (19)
N1—C1—C2—C7	-4.06 (18)	O1—S1—C14—F1	63.94 (16)
C1—C2—C3—C4	0.35 (19)	O2—S1—C14—F1	-175.28 (14)
C7—C2—C3—C4	-178.00 (12)	O3—S1—C14—F1	-55.02 (16)
C2—C3—C4—C5	-0.7 (2)	O1—S1—C14—F3	-174.22 (13)
C2—C3—C4—C8	178.79 (13)	O2—S1—C14—F3	-53.45 (15)
C3—C4—C5—C6	0.2 (2)	O3—S1—C14—F3	66.82 (14)
C8—C4—C5—C6	-179.25 (13)	O1—S1—C14—F2	-55.81 (13)
C4—C5—C6—C1	0.5 (2)	O2—S1—C14—F2	64.97 (13)
C4—C5—C6—C9	-179.79 (14)	O3—S1—C14—F2	-174.77 (11)
C2—C1—C6—C5	-0.90 (19)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C11—H11A $\cdots$ O1 <sup>i</sup>	0.98	2.56	3.477 (2)	155
C12—H12A $\cdots$ F2 <sup>ii</sup>	0.98	2.69	3.3859 (18)	129
C13—H13A $\cdots$ O1 <sup>i</sup>	0.98	2.45	3.3789 (18)	159
C13—H13B $\cdots$ O2 <sup>iii</sup>	0.98	2.29	3.2377 (18)	162
C13—H13C $\cdots$ O3	0.98	2.52	3.1723 (17)	124

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