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# Dimethylphenylsulfonium trifluoromethanesulfonate and methyldiphenylsulfonium trifluoromethanesulfonate

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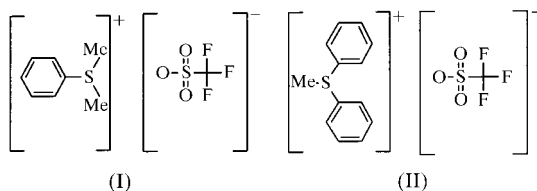
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The bonding geometry of sulfur in the cations of the title compounds,  $C_8H_{11}S^+ \cdot CF_3SO_3^-$  and  $C_{13}H_{13}S^+ \cdot CF_3SO_3^-$ , respectively, is similar and is independent of the ratio of the Me/Ph substituents. As expected, in both cations, the S—Ph bonds are somewhat shorter than the S—Me bonds. In both crystal structures, the interaction between cations and anions is similar.

## Comment

Sulfonium salts are known as photo acid generators (PAG). Their DUV-irradiation leads to decomposition and the formation of acid (Dektar & Hacker, 1990). Therefore, sulfonium salts have found a wide range of uses in UV-curing technologies, microlithography, holography and other photo-optical applications (Ito, 1999). The bonding geometry of sulfur in the cations of the title compounds, (I) and (II), is similar and is independent of the ratio of the Me/Ph substituents. As expected, in both cations, the S—Ph bonds [1.783 (2)–1.784 (2) Å] are somewhat shorter than the S—Me bonds [1.786 (2)–1.792 (2) Å]. In both crystal structures, the interaction between cations and anions is similar; the  $SO_3$  side of the anions form contacts preferentially with the methyl groups of the cations and correspondingly the  $CF_3$  side forms contacts with the phenyl groups.



## Experimental

Preparation of dimethylphenylsulfonium trifluoromethanesulfonate, (I): in accordance with Saeva & Morgan (1984), phenyl methyl sulfide (6.2 g, 50 mmol) was dissolved in methylene chloride (40 ml). Methyl trifluoromethanesulfonate (10.0 g, 60.0 mmol) was added dropwise at 273 K. The mixture was refluxed for 8 h, cooled for 8 h and poured into diethyl ether (150 ml). The product crystallized and was collected by filtration and air dried. Recrystallization from isopropyl alcohol gave 12.7 g (88% yield) of the pure product; m.p. 382 K;  $^1H$  NMR (methanol- $d_4$ ):  $\delta$  3.31 (s, 6H), 7.70–8.15 (m, 5H); elemental analysis for  $C_9H_{11}F_3O_3S_2$ , calculated/found: C 37.48/37.48, H 3.99/3.89 and S 22.45/22.26%. Preparation of methyldiphenylsulfonium trifluoromethanesulfonate, (II): to a solution of diphenyl sulfide (9.3 g, 50 mmol) in methylene chloride (40 ml), methyl trifluoromethanesulfonate (10.0 g, 60 mmol) was added. The mixture was refluxed for 8 h and stirred for a further 8 h at room temperature. After crystallization from isopropyl alcohol, 15.5 g (88% yield) of the desired product were obtained; m.p. 370 K;  $^1H$  NMR (methanol- $d_4$ ):  $\delta$  3.80 (s, 3H), 7.70–8.15 (m, 10H); elemental analysis for  $C_{14}H_{13}F_3O_3S_2$ , calculated/found: C 47.98/47.99, H 3.74/3.84 and S 18.31/18.59%.

## Compound (I)

### Crystal data

$C_8H_{11}S^+ \cdot CF_3SO_3^-$   
 $M_r = 288.30$   
 Monoclinic,  $P2_1/c$   
 $a = 13.659$  (2) Å  
 $b = 10.045$  (2) Å  
 $c = 9.4366$  (16) Å  
 $\beta = 108.205$  (18)°  
 $V = 1229.9$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.557$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2000 reflections  
 $\theta = 2.5$ – $25.0^\circ$   
 $\mu = 0.464$  mm<sup>-1</sup>  
 $T = 180$  (2) K  
 Block, colorless  
 $0.84 \times 0.60 \times 0.40$  mm

### Data collection

Stoe IPDS diffractometer  
 $\varphi$ -rotation,  $\varphi$ -incr. =  $1.6^\circ$ , 138 exposure scans  
 Absorption correction: reldelf  
 (ABSCOR; Stoe & Cie, 1997)  
 $T_{min} = 0.697$ ,  $T_{max} = 0.836$   
 7424 measured reflections

2221 independent reflections  
 1975 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.072$   
 $\theta_{max} = 25.5^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -12 \rightarrow 12$   
 $l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.125$   
 $S = 1.056$   
 2221 reflections  
 156 parameters  
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.7631P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.007$   
 $\Delta\rho_{max} = 0.89$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.44$  e Å<sup>-3</sup>

## Compound (II)

### Crystal data

$C_{13}H_{13}S^+ \cdot CF_3SO_3^-$   
 $M_r = 350.36$   
 Monoclinic,  $P2_1/c$   
 $a = 12.5122$  (13) Å  
 $b = 9.0284$  (6) Å  
 $c = 15.3932$  (14) Å  
 $\beta = 113.552$  (8)°  
 $V = 1594.0$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.460$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 116 reflections  
 $\theta = 14.1$ – $15.0^\circ$   
 $\mu = 0.373$  mm<sup>-1</sup>  
 $T = 180$  (2) K  
 Block, colorless  
 $0.98 \times 0.76 \times 0.50$  mm

## Data collection

Stoe Stadi-4 diffractometer  
 $2\theta/\omega$  scans, ratio = 1.0, width ( $\omega$ ) =  
 1.35–1.50°  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.712$ ,  $T_{\max} = 0.836$   
 5742 measured reflections  
 3480 independent reflections  
 3137 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 27.03^\circ$   
 $h = -16 \rightarrow 16$   
 $k = 0 \rightarrow 11$   
 $l = -19 \rightarrow 19$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 2.4%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.082$   
 $S = 1.066$   
 3480 reflections  
 252 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.6612P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.007$   
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0108 (12)

For (I), a  $\Delta F^2$ -based absorption correction was carried out. The calculation was performed with *ABSCOR* (Stoe & Cie, 1997), a modification of *DIFABS* (Walker & Stuart, 1983). In contrast to *DIFABS*, *ABSCOR* works with  $F^2$  values instead of  $F$ . For (II), a  $\psi$ -

scan-related absorption correction was carried out (North *et al.*, 1968).

For compound (II), data collection: *IPDS-2.87* (Stoe & Cie, 1997); cell refinement: *IPDS-2.87*; data reduction: *IPDS-2.87*. For compound (II), data collection: *STADIA-1.06* (Stoe & Cie, 1997); cell refinement: *STADIA-1.06*; data reduction: *XRED-1.07* (Stoe & Cie, 1997). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSTEP-2.18* (Stoe & Cie, 1997); software used to prepare material for publication: *SHELXL97*.

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