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(*Z*)-2-Methylbuten-1-yl(aryl)iodonium trifluoromethanesulfonates containing electron-withdrawing groups on the aryl moiety

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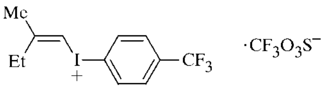
The crystal structures of [(*Z*)-2-methylbut-1-en-1-yl][4-(trifluoromethyl)phenyl]iodonium trifluoromethanesulfonate, $C_{12}H_{13}F_3I^+\cdot CF_3O_3S^-$, (I), (3,5-dichlorophenyl)[(*Z*)-2-methylbut-1-en-1-yl]iodonium trifluoromethanesulfonate, $C_{11}H_{12}Cl_2I^+\cdot CF_3O_3S^-$, (II), and bis{[3,5-bis(trifluoromethyl)phenyl][(*Z*)-2-methylbut-1-en-1-yl]iodonium} bis(trifluoromethanesulfonate) dichloromethane solvate, $2C_{13}H_{12}F_6I^+\cdot 2CF_3O_3S^-\cdot CH_2Cl_2$, (III), are described. Neither simple acyclic β,β-dialkyl-substituted alkenyl(aryl)idonium salts nor a series containing electron-deficient aryl rings have been described prior to this work. Compounds (I)–(III) were found to have distorted square-planar geometries, with each I atom interacting with two trifluoromethanesulfonate counter-ions.

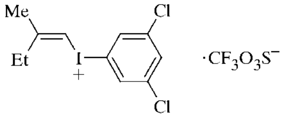
Comment

We have recently shown that alkenyl(aryl)iodonium trifluoromethanesulfonate salts are highly reactive in fragmentation reactions and that an increase in the effective electron-withdrawing nature of the aryl ring increases reactivity (Hinkle & Thomas, 1997; Hinkle *et al.*, 1999; McNeil *et al.*, 2001). In this regard, alkenyl(aryl)iodonium salts are known to be highly reactive alkenyl halide equivalents. The phenyliodonio compounds react 10^6 times faster in solvolysis experiments than the corresponding trifluoromethanesulfonates (Okuyama *et al.*, 1995). This enhanced reactivity could potentially lead to a variety of new reactions. In fact, alkenyl(phenyl)iodonium tetrafluoroborates are known to be electrophiles in vinylic S_N2 substitution reactions (Okuyama *et al.*, 1998, 2001). It was hoped that the increased reactivity of salts containing electron-withdrawing groups on the aromatic ring would lead to vinylic C—I bond elongation proportional to the reactivity. Herein, we report the structures of three different alkenyl(aryl)iodonium trifluoromethanesulfonates, the title compounds (I), (II) and (III), which show that the structures do not display this relationship.

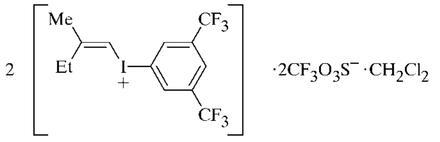
The alkenyl(aryl)iodonium salts (I)–(III) were obtained by the reaction of 'iodonium transfer' reagents (Zhdankin *et al.*, 1993) with stereoisomerically pure (*Z*)-2-methylbut-1-en-1-yltributylstannane and crystallized from CH_2Cl_2 by diffusion of pentane. Compound (I) provided monoclinic crystals, whereas both (II) and (III) were triclinic. The crystal of (I) (Fig. 1) contains a single dimeric unit, whereas crystals of (II) (Figs. 2 and 3) and (III) (Figs. 4 and 5) each contain two crystallographically independent dimeric units.



(I)



(II)



(III)

Previously, many iodonium salt structures have been described, including only the closest contact trifluoromethanesulfonate interaction, and have been designated as 'T-shaped' trigonal-bipyramidal geometries in which the vinylic moiety occupies an equatorial position relative to I, whereas the phenyl moiety and trifluoromethanesulfonate counter-ion are axial. If one considers only the interaction between the closest trifluoromethanesulfonate anion and the I atom, salts (I)–(III) reveal trigonal-bipyramidal geometries about the cationic I atom. In this sense, these salts are considered hypervalent 8-I-2 derivatives of iodine in the Martin–Arduengo formalism (Perkins *et al.*, 1980). This geometry is typical of 8-I-2 iodonium compounds, whether they are diaryl-, alkynyl- or alkenyl(aryl)iodonium salts (Varvoglis, 1992; Stang & Zhdankin, 1996).

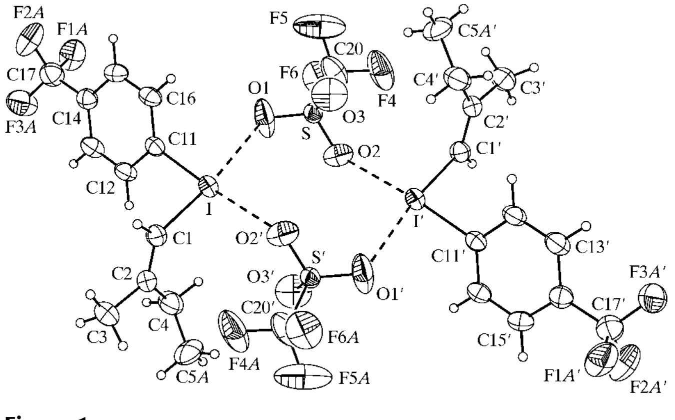


Figure 1
A view of the cyclic unit of (I) formed from two iodonium and two trifluoromethanesulfonate ions. The cyclic unit is formed about the crystallographic inversion center $(0,0,\frac{1}{2})$ and primed atoms are related to unprimed atoms *via* this inversion center. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Each unit cell for (I)–(III) contains two alkenyl(aryl)iodonium trifluoromethanesulfonates which are held in a dimeric arrangement about the I centers, giving the iodonium salts distorted square-planar geometries, rather than trigonal pyramidal as described above. The positively charged I atom interacts simultaneously with both trifluoromethanesulfonates, although contact is slightly closer to one of the two. For instance, in one dimer of compound (III), the distance between the I atom and the closest O atom of a trifluoromethanesulfonate anion is 2.767 (2) Å, whereas the distance to the other trifluoromethanesulfonate anion is 2.985 (3) Å. It should be noted that the other crystallographically independent iodonium dimer found for (III) contains more uniform iodine–trifluoromethanesulfonate distances. These bond lengths were found to be 2.893 (3) and 2.881 (2) Å. This variation in non-bonded distances is likely to be due to crystal-packing forces rather than any electronic effects. Square-planar geometry has been described by several investigators

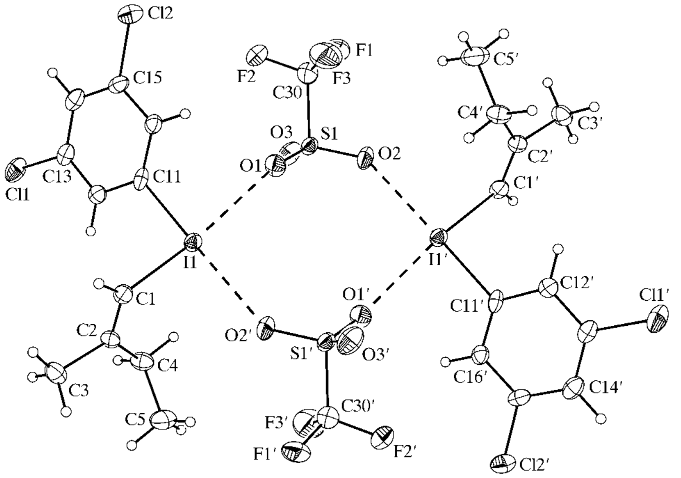


Figure 2
A view illustrating the interactions between the first crystallographically independent iodonium ion and the nearby trifluoromethanesulfonate ions in (II), and the cyclic unit thereby formed. Primed atoms are related to unprimed atoms *via* the crystallographic inversion center (0,0,0). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

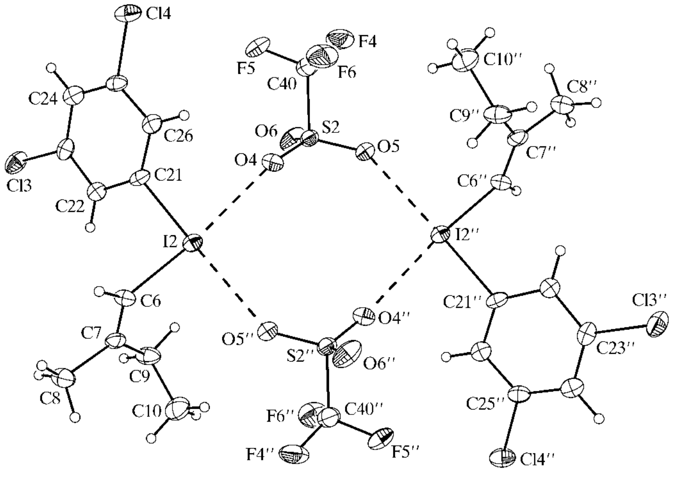


Figure 3
A view illustrating the second crystallographically independent iodonium ion in (II), the nearby trifluoromethanesulfonate ions and the cyclic unit thereby formed. Double-primed atoms are related to unprimed atoms *via* the crystallographic inversion center ($\frac{1}{2}$,0,$\frac{1}{2}$). Note that there are no interactions between this iodonium ion and the trifluoromethanesulfonate counter-ion associated with the other iodonium ion, or *vice versa* (Fig. 2). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

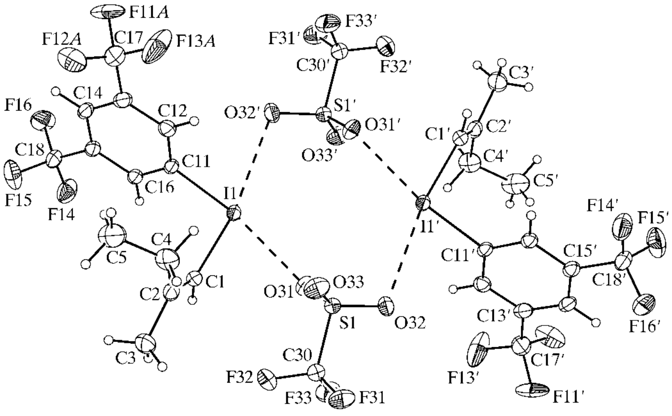


Figure 4
A view illustrating the interactions between the first crystallographically independent iodonium ion and the nearby trifluoromethanesulfonate ions in (III), and the cyclic unit thereby formed. Primed atoms are related to unprimed atoms *via* the crystallographic inversion center ($\frac{1}{2}$,$\frac{1}{2}$,0). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dichloromethane solvate has been omitted for clarity.

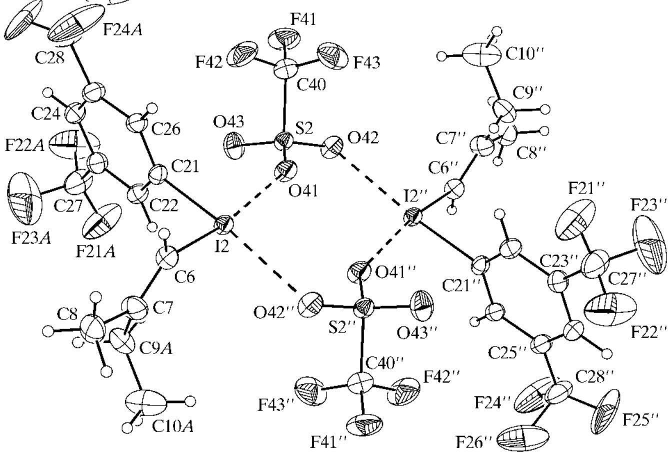


Figure 5
A view illustrating the interactions between the second crystallographically independent iodonium ion and the nearby trifluoromethanesulfonate ions in (III), and the cyclic unit thereby formed. Double-primed atoms are related to unprimed atoms *via* the crystallographic inversion center (0,$\frac{1}{2}$,0). Note that there are no interactions between this iodonium ion and the trifluoromethanesulfonate counter-ions associated with the iodonium ion shown in Fig. 4. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dichloromethane solvate has been omitted for clarity.

(*e.g.* Gately *et al.*, 1992; Kasumov *et al.*, 1996, 1997) and was most recently observed in the case of a (2,2′-bithio-5-phenyl)(phenyl)iodonium trifluoromethanesulfonate (Tykwinski *et al.*, 2000).

Despite the different electron-withdrawing substituents on the aryliodonio moiety, there is little structural difference within the covalently bonded moieties of the three compounds. The vinylic C—C bond lengths range from 1.293 (5) to 1.326 (5) Å for (III), with the corresponding values for (I) and (II) being in between. However, given the experimental uncertainties, the bond-length differences are inconsequential. The C—I bond lengths between the aryl rings and vinylic C atoms, at approximately 2.1 Å, are typical of those for iodonium salts (Varvoglis, 1992; Stang & Zhdankin, 1993).

The incorporation of increasingly electron-withdrawing aryliodonio moieties (Lowry & Richardson, 1987) results in another slight structural variation. The non-bonded distance between the I atom and the closest trifluoromethanesulfonate counter-ion is longest [2.909 (6) Å] in (I), the compound with the least electron-deficient aromatic ring. In one of the two dimeric units of (II) and (III), the I···O distance decreases to 2.802 (6) and 2.767 (2) Å for (II) and (III), respectively. However, this shortening is not observed in the second dimer of each. Consequently, this variation is also likely to be simply a manifestation of crystal-packing forces. The sum of the covalent radii of I and O is 2.08 Å and the sum of their van der Waals radii is 3.45 Å (Huheey *et al.*, 1993).

Experimental

The three title complexes were prepared as previously described by Hinkle *et al.* (1999) and were crystallized from CH_2Cl_2 solutions layered with pentane in 1 dram vials. These vials were kept at 258 K for 24–72 h before the solvent was decanted.

Compound (I)

Crystal data

$C_{12}H_{13}F_3I^+\cdot CF_3O_3S^-$
$M_r = 490.19$
Monoclinic, $P2_1/n$
$a = 6.5676\ (7)$ Å
$b = 17.2459\ (18)$ Å
$c = 15.7394\ (16)$ Å
$\beta = 96.803\ (10)^\circ$
$V = 1770.2\ (3)$ Å^3
$Z = 4$

$D_x = 1.839$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5559 reflections
$\theta = 2.4$–26.4°
$\mu = 1.99$ mm^{-1}
$T = 193\ (2)$ K
Prism, colorless
$0.33 \times 0.22 \times 0.13$ mm

Data collection

Bruker *P*4/RA/SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.601$, $T_{max} = 0.772$
8591 measured reflections
3622 independent reflections
2912 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 26.4^\circ$
$h = -8 \rightarrow 3$
$k = -21 \rightarrow 21$
$l = -19 \rightarrow 18$
169 standard reflections
frequency: 1110 min
intensity decay: <1%

Table 1
Selected geometric parameters (Å, °) for (I).

I—C1	2.086 (6)	C4—C5*B*	1.39 (2)
I—O1	2.909 (6)	S—O1	1.391 (5)
I—O2^i	2.991 (8)	S—O2	1.403 (6)
I—C11	2.106 (6)	S—O3	1.405 (6)
C1—C2	1.319 (8)	S—C20	1.794 (9)
C2—C3	1.502 (9)	F4—C20	1.321 (11)
C2—C4	1.503 (10)	F5—C20	1.378 (14)
C4—C5*A*	1.429 (16)	F6—C20	1.268 (10)
O1—I—O2^i	105.86 (19)	O1—S—O2	110.9 (5)
O1—I—C1	171.2 (2)	O1—S—O3	122.4 (5)
O1—I—C11	76.64 (18)	O2—S—O3	109.6 (5)
O2^i—I—C1	82.9 (2)	O1—S—C20	104.2 (4)
O2^i—I—C11	168.2 (2)	O2—S—C20	102.9 (6)
C1—I—C11	94.9 (2)	O3—S—C20	104.7 (4)
I—C1—C2	124.2 (5)	I—O1—S	114.7 (3)
C1—C2—C3	117.4 (6)	S—C20—F4	112.4 (7)
C1—C2—C4	126.0 (6)	S—C20—F5	109.0 (8)
C3—C2—C4	116.6 (6)	S—C20—F6	115.5 (7)
C2—C4—C5*A*	115.3 (9)	F4—C20—F5	106.4 (9)
C2—C4—C5*B*	120.4 (12)	F4—C20—F6	109.7 (9)
I—C11—C12	118.3 (4)	F5—C20—F6	103.0 (9)
I—C11—C16	120.2 (4)		

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.144$
$S = 1.04$
3622 reflections
256 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2 + 3.5701P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.40$ e Å^{-3}
$\Delta\rho_{min} = -1.16$ e Å^{-3}

Compound (II)

Crystal data

$C_{11}H_{12}Cl_2I^+\cdot CF_3O_3S^-$
$M_r = 491.08$
Triclinic, $P\overline{1}$
$a = 9.1705\ (10)$ Å
$b = 13.4357\ (15)$ Å
$c = 15.6030\ (17)$ Å
$\alpha = 69.245\ (10)^\circ$
$\beta = 88.342\ (10)^\circ$
$\gamma = 74.358\ (10)^\circ$
$V = 1726.4\ (3)$ Å^3

$Z = 4$
$D_x = 1.889$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4172 reflections
$\theta = 2.6$–26.4°
$\mu = 2.32$ mm^{-1}
$T = 193\ (2)$ K
Prism, colorless
$0.49 \times 0.07 \times 0.04$ mm

Data collection

Bruker PLATFORM/SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1997*a*)
$T_{min} = 0.559$, $T_{max} = 0.922$
8587 measured reflections
6950 independent reflections

4412 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 26.5^\circ$
$h = -10 \rightarrow 11$
$k = -16 \rightarrow 14$
$l = -19 \rightarrow 10$
3 standard reflections
frequency: 960 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.152$
$S = 0.96$
6950 reflections
399 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.07$ e Å^{-3}
$\Delta\rho_{min} = -1.21$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

I1—O1	2.848 (6)	C9—C10	1.510 (14)
I1—O2^{i}	2.802 (6)	S1—O1	1.432 (6)
I1—C1	2.106 (8)	S1—O2	1.436 (6)
I1—C11	2.119 (8)	S1—O3	1.426 (7)
C1—C2	1.297 (11)	S1—C30	1.819 (11)
C2—C3	1.525 (11)	F1—C30	1.330 (13)
C2—C4	1.503 (11)	F2—C30	1.345 (11)
C4—C5	1.520 (13)	F3—C30	1.299 (13)
I2—O4	2.832 (6)	S2—O4	1.431 (6)
I2—O5^{ii}	2.850 (6)	S2—O5	1.443 (6)
I2—C6	2.098 (8)	S2—O6	1.430 (6)
I2—C21	2.127 (8)	S2—C40	1.822 (10)
C6—C7	1.313 (12)	F4—C40	1.319 (11)
C7—C8	1.524 (12)	F5—C40	1.327 (11)
C7—C9	1.492 (12)	F6—C40	1.349 (11)
O1—I1—O2^{i}	98.49 (18)	O1—S1—O2	114.5 (4)
O1—I1—C1	173.8 (3)	O1—S1—O3	115.2 (4)
O1—I1—C11	80.9 (3)	O2—S1—O3	115.3 (4)
O2^{i}—I1—C1	87.1 (3)	O1—S1—C30	102.4 (5)
O2^{i}—I1—C11	179.0 (3)	O2—S1—C30	102.5 (4)
C1—I1—C11	93.5 (3)	O3—S1—C30	104.5 (5)
I1—C1—C2	122.6 (6)	I1—O1—S1	151.5 (4)
C1—C2—C3	117.2 (8)	S1—C30—F1	111.1 (8)
C1—C2—C4	127.0 (8)	S1—C30—F2	110.1 (7)
C3—C2—C4	115.8 (7)	S1—C30—F3	112.8 (8)
C2—C4—C5	113.5 (8)	F1—C30—F2	107.1 (9)
I1—C11—C12	119.1 (6)	F1—C30—F3	107.3 (9)
I1—C11—C16	117.6 (6)	F2—C30—F3	108.1 (9)
O4—I2—O5^{ii}	98.26 (18)	O4—S2—O5	114.8 (4)
O4—I2—C6	174.1 (3)	O4—S2—O6	115.3 (4)
O4—I2—C21	80.6 (3)	O4—S2—C40	102.9 (4)
O5^{ii}—I2—C6	87.4 (3)	O5—S2—O6	115.0 (4)
O5^{ii}—I2—C21	178.6 (3)	O5—S2—C40	102.6 (4)
C6—I2—C21	93.7 (3)	O6—S2—C40	103.8 (4)
I2—C6—C7	122.7 (7)	I2—O4—S2	154.4 (4)
C6—C7—C8	118.0 (8)	S2—C40—F4	112.4 (7)
C6—C7—C9	127.0 (8)	S2—C40—F5	111.3 (7)
C8—C7—C9	114.9 (8)	S2—C40—F6	111.1 (7)
C7—C9—C10	112.9 (8)	F4—C40—F5	108.8 (8)
I2—C21—C22	118.0 (6)	F4—C40—F6	106.7 (8)
I2—C21—C26	117.7 (6)	F5—C40—F6	106.3 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$.

Compound (III)

Crystal data

$2C_{13}H_{12}F_6I^+ \cdot 2CF_3O_3S^- \cdot CH_2Cl_2$
$M_r = 1201.32$
Triclinic, $P\overline{1}$
$a = 12.5807$ (13) Å
$b = 13.2381$ (14) Å
$c = 13.6567$ (14) Å
$\alpha = 81.854$ (10)°
$\beta = 72.429$ (10)°
$\gamma = 79.851$ (10)°
$V = 2124.9$ (4) Å^3
$Z = 2$
$D_x = 1.878$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.3$–26.3°
$\mu = 1.82$ mm^{-1}
$T = 193$ (2) K
Prism, colorless
0.39 × 0.17 × 0.12 mm

Data collection

Bruker *P*4/RA/SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 1997*a*)
$T_{min} = 0.629$, $T_{max} = 0.857$
12 749 measured reflections
8628 independent reflections
6911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.4°$
$h = -13 \rightarrow 15$
$k = -13 \rightarrow 16$
$l = -17 \rightarrow 17$
185 standard reflections
frequency: 1470 min
intensity decay: <1%

Table 3
Selected geometric parameters (Å, °) for (III).

I1—O31	2.767 (2)	C9*A*—C10*A*	1.481 (11)
I1—O32^{i}	2.985 (3)	C9*B*—C10*B*	1.54 (2)
I1—C1	2.093 (3)	S1—O31	1.441 (2)
I1—C11	2.111 (3)	S1—O32	1.443 (2)
C1—C2	1.326 (5)	S1—O33	1.426 (3)
C2—C3	1.508 (5)	S1—C30	1.815 (4)
C2—C4	1.504 (6)	F31—C30	1.333 (4)
C4—C5	1.524 (6)	F32—C30	1.319 (4)
I2—O41	2.881 (2)	F33—C30	1.318 (5)
I2—O42^{ii}	2.893 (3)	S2—O41	1.443 (2)
I2—C6	2.094 (3)	S2—O42	1.442 (3)
I2—C21	2.104 (3)	S2—O43	1.435 (3)
C6—C7	1.293 (5)	S2—C40	1.812 (4)
C7—C8	1.500 (5)	F41—C40	1.334 (5)
C7—C9*A*	1.559 (9)	F42—C40	1.319 (5)
C7—C9*B*	1.512 (15)	F43—C40	1.319 (5)
O31—I1—O32^{i}	115.02 (7)	I2—C21—C26	119.4 (2)
O31—I1—C1	75.04 (10)	O31—S1—O32	113.82 (15)
O31—I1—C11	170.49 (10)	O31—S1—O33	114.71 (16)
O32^{i}—I1—C1	169.94 (10)	O31—S1—C30	104.05 (17)
O32^{i}—I1—C11	74.41 (10)	O32—S1—O33	115.31 (17)
C1—I1—C11	95.52 (12)	O32—S1—C30	103.24 (16)
I1—C1—C2	123.0 (3)	O33—S1—C30	103.67 (19)
C1—C2—C3	117.7 (4)	I1—O31—S1	126.92 (14)
C1—C2—C4	125.9 (3)	S1—C30—F31	110.3 (3)
C3—C2—C4	116.4 (3)	S1—C30—F32	111.5 (3)
C2—C4—C5	113.0 (4)	S1—C30—F33	111.3 (3)
I1—C11—C12	118.6 (2)	F31—C30—F32	108.5 (3)
I1—C11—C16	118.7 (2)	F31—C30—F33	106.8 (3)
O41—I2—O42^{ii}	106.24 (7)	F32—C30—F33	108.3 (3)
O41—I2—C6	172.58 (10)	O41—S2—O42	113.58 (15)
O41—I2—C21	78.73 (10)	O41—S2—O43	115.53 (17)
O42^{ii}—I2—C6	80.17 (11)	O41—S2—C40	103.44 (18)
O42^{ii}—I2—C21	174.69 (10)	O42—S2—O43	115.20 (17)
C6—I2—C21	94.99 (13)	O42—S2—C40	103.00 (18)
I2—C6—C7	124.9 (3)	O43—S2—C40	103.86 (19)
C6—C7—C8	118.2 (4)	I2—O41—S2	149.20 (16)
C6—C7—C9*A*	125.2 (4)	S2—C40—F41	110.0 (3)
C6—C7—C9*B*	119.7 (6)	S2—C40—F42	111.4 (3)
C8—C7—C9*A*	115.1 (4)	S2—C40—F43	111.3 (3)
C8—C7—C9*B*	113.7 (6)	F41—C40—F42	107.8 (4)
C7—C9*A*—C10*A*	110.9 (8)	F41—C40—F43	107.8 (4)
C7—C9*B*—C10*B*	102.5 (15)	F42—C40—F43	108.4 (4)
I2—C21—C22	118.6 (2)		

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, 1 - y, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.078$
$S = 0.97$
8628 reflections
618 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

H atoms were treated as riding, with C—H = 0.95–0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. For (I), the CF_3 group was found to be rotationally disordered. Thus, two sets of three F atoms each (with occupancy factors of 60% for F1*A*, F2*A* and F3*A*, and 40% for F1*B*, F2*B* and F3*B*) were refined. For this compound, the terminal C atom of the 2-methyl-1-butenyl group was determined to be disordered over two positions (C5*A* 55% and C5*B* 45%). The largest residual peaks of electron density (1.40 and −1.16 e Å^{-3}) were found within 0.81 Å of the I atom. For (II), the largest residual peaks of electron density (2.07 and −1.21 e Å^{-3}) were found within 0.94 Å of one of the I atoms (I1). For (III), one of the CF_3 groups on the phenyl ring attached to I1 was found to be rotationally disordered. Thus, two sets of three F atoms each (with occupancy factors of 70% for F11*A*, F12*A* and F13*A*, and 30% for F11*B*, F12*B* and F13*B*) were refined. Also for (III), both of the CF_3 groups on the phenyl ring attached to I2 displayed a rotational disorder, such that each was refined with two sets of three F atoms (F21*A*, F22*A* and F23*A*, and F21*B*, F22*B* and F23*B* attached to C27, and F24*A*, F25*A* and F26*A*, and F24*B*, F25*B* and F26*B* attached to C28), each set with an occupancy factor of 50%. For (III), the two terminal butenyl C atoms of the 2-methyl-1-butenyl group attached to I2 were refined as two sets of positions (C9*A* and C10*A* at 66.67% occupancy, and C9*B* and C10*B* at 33.33% occupancy). The largest residual peaks of electron density (0.49 and -0.64 e Å^{-3}) were found within 1.06 Å of one of the Cl atoms (Cl2*S*) of the dichloromethane molecule.

For all three compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997*a*). For compounds (I) and (III), program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); for compound (II), program(s) used to solve structure: *DIRDIF*96 (Beurskens *et al.*, 1996). For all three compounds, program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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