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trans-2-Fluorocyclohexyl *p*-Toluenesulfonate and *trans*-2-Fluorocycloheptyl *p*-Toluenesulfonate

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Abstract

The title compounds, $C_{13}H_{17}FO_3S$ and $C_{14}H_{19}FO_3S$, have *trans* configurations with long distances between the F and sulfonyl O atoms. Some disorder was found in the cycloheptyl group.

Comment

Both title compounds, *trans*-2-fluorocyclohexyl *p*-toluenesulfonate, (I), and *trans*-2-fluorocycloheptyl *p*-toluenesulfonate, (II), are obtained by the action of tosyl chloride on *trans*-fluorohydrines (Baklouti & El-Gharbi, 1979). They constitute a class of compounds

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† Deceased 24th October 1993.

from which it is possible to synthesize quite a large variety of other monofluorinated products by substitution of the *p*-toluenesulfonate group (Toulgui, Chaabouni & Baklouti, 1990).

(I)

(II)
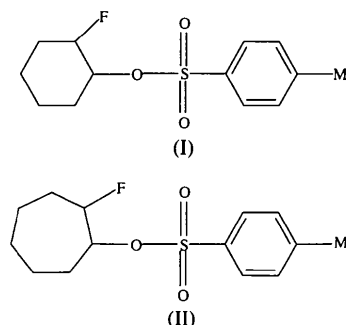
The identification of the two *trans*-2-fluorocycloalkyl *p*-toluenesulfonates, (I) and (II), was made from IR, ^1H NMR and ^{19}F NMR spectra, and mass spectroscopy measurements. From dynamic ^{19}F NMR, it was established that, in solution, the compounds adopt *trans* configurations; however, the spacial arrangement of the tosyl group relative to the fluorocycloalkyl moiety could not be determined without X-ray structure analysis. This investigation has shown that for the two title compounds, the more stable conformation is characterized by the longest distance between the F atoms and the O atoms of the sulfonyl moiety.

The average C—C distance is 1.378 (8) Å in the aromatic rings of the two compounds and 1.511 (5) Å in the cyclohexyl group of compound (I). As described elsewhere (Dupont *et al.*, 1991; Geetha & Rajan, 1991), some disorder was observed in the cycloheptyl group: one C—C bond distance (C6—C7) is 1.298 (15) Å, whereas the other six are comparable, in the range 1.487 (17)–1.521 (12) Å.
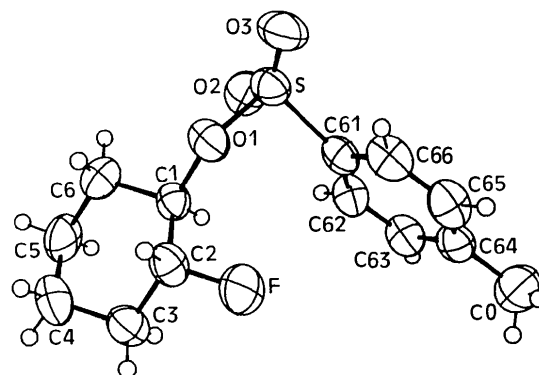

Fig. 1. *ORTEP*II (Johnson, 1971) view of compound (I) with the atomic numbering and 50% probability displacement ellipsoids for non-H atoms. H atoms are shown as small spheres of arbitrary radii.

In both compounds, the arrangement of the O atoms around the S atom is approximately tetrahedral; the bond angles and distances between this atom and those occupying the tetrahedral vertices are comparable (see Table 3). The C—S—O—C torsion angles are −76.4 (2) and 72.5 (5)° for (I) and (II), respectively.

The 2-fluorocyclohexyl p-toluenesulfonate molecule is almost identical to that of cyclohexyl p-toluene-sulfonate (James & McConnell, 1971).
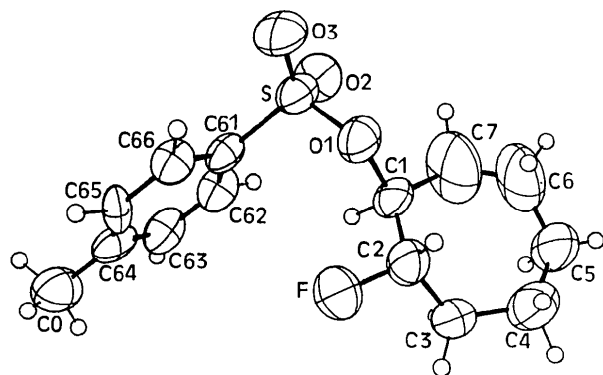

Fig. 2. *ORTEP*II (Johnson, 1971) view of compound (II) with the atomic numbering. Displacement ellipsoids and H atoms as in Fig. 1.

Experimental

Compound (I)

Crystal data

$C_{13}H_{17}FO_3S$
$M_r = 272.3$
Monoclinic
$P2_1$
$a = 7.346\,(1)$ Å
$b = 5.870\,(2)$ Å
$c = 15.959\,(3)$ Å
$\beta = 99.64\,(1)°$
$V = 678.4\,(5)$ Å^3
$Z = 2$
$D_x = 1.33$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.2–14.0°$
$\mu = 0.24$ mm^{-1}
$T = 300$ K
Prism
$0.60 \times 0.28 \times 0.14$ mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3882 measured reflections
1454 independent reflections
1284 observed reflections
[$I > 2.5\sigma(I)$]

$R_{int} = 0.025$
$\theta_{max} = 25°$
$h = -9 \rightarrow 9$
$k = -7 \rightarrow 7$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.029$
$wR = 0.032$

$w = 1.27/[\sigma^2(F)$
$+ 0.00038F^2]$
$(\Delta/\sigma)_{max} = 0.31$

$S = 1.1$
1284 reflections
215 parameters
Only coordinates of H atoms refined

$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
F	0.2837 (3)	0.3013 (5)	0.3025 (1)	0.095 (2)
S	0.6652 (1)	0.6190	0.2252	0.058 (4)
O1	0.4544 (2)	0.5713 (3)	0.1940 (1)	0.059 (1)
O2	0.7724 (3)	0.4857 (5)	0.1769 (1)	0.072 (1)
O3	0.6781 (3)	0.8612 (4)	0.2238 (2)	0.085 (2)
C0	0.8148 (5)	0.2973 (10)	0.5888 (2)	0.085 (3)
C1	0.3927 (3)	0.3374 (5)	0.1728 (2)	0.047 (1)
C2	0.2272 (4)	0.2969 (6)	0.2140 (2)	0.057 (1)
C3	0.1418 (5)	0.0660 (6)	0.1899 (2)	0.064 (2)
C4	0.0908 (5)	0.0458 (8)	0.0942 (2)	0.077 (2)
C5	0.2575 (6)	0.0833 (8)	0.0529 (2)	0.079 (2)
C6	0.3446 (6)	0.3147 (8)	0.0770 (2)	0.073 (2)
C61	0.7064 (3)	0.5251 (5)	0.3307 (2)	0.051 (2)
C62	0.7870 (4)	0.3155 (5)	0.3507 (2)	0.058 (2)
C63	0.8195 (4)	0.2453 (6)	0.4340 (2)	0.061 (2)
C64	0.7728 (3)	0.3780 (6)	0.4987 (2)	0.058 (2)
C65	0.6905 (4)	0.5854 (6)	0.4768 (2)	0.066 (2)
C66	0.6568 (4)	0.6610 (5)	0.3943 (2)	0.061 (2)

Compound (II)

Crystal data

$C_{14}H_{19}FO_3S$
$M_r = 286.37$
Orthorhombic
$P2_12_12_1$
$a = 6.022\,(1)$ Å
$b = 7.319\,(1)$ Å
$c = 32.279\,(5)$ Å
$V = 1422.7\,(7)$ Å^3
$Z = 4$
$D_x = 1.33$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.4–13.6°$
$\mu = 0.23$ mm^{-1}
$T = 300$ K
Trapezoidal
$0.35 \times 0.15 \times 0.07$ mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3472 measured reflections
1197 independent reflections
819 observed reflections
[$I > 3\sigma(I)$]

$R_{int} = 0.02$
$\theta_{max} = 26°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 35$
3 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.044$
$wR = 0.046$
$S = 1.6$
819 reflections
194 parameters
Only coordinates of H atoms refined

$w = 1.69/[\sigma^2(F)$
$+ 0.00052F^2]$
$(\Delta/\sigma)_{max} = 0.18$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
F	−0.1442 (9)	0.4238 (6)	0.0957 (1)	0.119 (4)
S	0.1995 (3)	0.0120 (3)	0.1285 (1)	0.065 (1)
O1	0.1352 (8)	0.2062 (6)	0.1442 (1)	0.076 (3)
O2	0.0905 (9)	−0.1231 (7)	0.1530 (2)	0.086 (4)
O3	0.4350 (7)	0.0138 (8)	0.1269 (2)	0.093 (4)
C0	−0.1610 (17)	−0.0423 (11)	−0.0457 (3)	0.093 (6)
C1	−0.0989 (13)	0.2475 (10)	0.1544 (2)	0.077 (5)
C2	−0.1385 (15)	0.4388 (10)	0.1389 (2)	0.076 (6)
C3	−0.3578 (13)	0.5215 (12)	0.1529 (2)	0.085 (6)
C4	−0.3555 (20)	0.6021 (13)	0.1956 (3)	0.103 (7)
C5	−0.3466 (18)	0.4707 (16)	0.2309 (3)	0.109 (7)
C6	−0.1713 (16)	0.3278 (16)	0.2297 (3)	0.142 (8)
C7	−0.1403 (26)	0.2141 (16)	0.1994 (3)	0.163 (9)
C61	0.0951 (10)	0.0002 (8)	0.0777 (2)	0.054 (3)
C62	−0.1099 (12)	−0.0784 (9)	0.0706 (2)	0.066 (5)
C63	−0.1889 (14)	−0.0883 (10)	0.0309 (3)	0.073 (5)
C64	−0.0690 (12)	−0.0231 (9)	−0.0025 (2)	0.068 (5)
C65	0.1354 (13)	0.0556 (9)	0.0057 (2)	0.055 (6)
C66	0.2189 (12)	0.0684 (8)	0.0451 (2)	0.059 (4)

Table 3. *Selected bond distances* (Å) *and angles* (°) *in compounds* (I) *and* (II)

	(I)	(II)
S—O1	1.570 (2)	1.558 (5)
S—O2	1.424 (2)	1.428 (6)
S—O3	1.426 (3)	1.419 (4)
S—C61	1.749 (3)	1.758 (7)
F—C2	1.405 (3)	1.399 (7)
C61—C62	1.380 (4)	1.381 (9)
C62—C63	1.374 (4)	1.369 (12)
C63—C64	1.381 (4)	1.383 (13)
C64—C65	1.378 (5)	1.385 (11)
C65—C66	1.371 (5)	1.370 (12)
C66—C61	1.387 (4)	1.382 (9)
C0–C64	1.496 (5)	1.507 (14)
C1—O1	1.468 (4)	1.479 (9)
C1—C2	1.495 (4)	1.506 (10)
C2—C3	1.516 (4)	1.521 (12)
C3—C4	1.515 (4)	1.499 (14)
C4—C5	1.501 (6)	1.492 (16)
C5—C6	1.523 (6)	1.487 (17)
C6—C1	1.516 (4)	–
C6—C7	–	1.298 (15)
C7—C1	–	1.494 (12)
O1—S—O2	109.6 (1)	109.7 (3)
O2—S—O3	119.7 (2)	119.0 (4)
O3—S—O1	103.8 (1)	104.6 (4)
C61—S—O1	104.6 (1)	105.0 (3)
C61—S—O2	109.0 (1)	108.6 (3)
C61—S—O3	109.1 (2)	109.0 (3)
S—O1—C1	119.4 (2)	119.7 (5)
S—C61—C62	120.2 (2)	119.6 (6)
S—C61—C66	120.0 (2)	119.9 (5)
C62—C61—C66	119.9 (3)	120.5 (7)
C61—C62—C63	119.4 (3)	119.1 (7)
C62—C63—C64	121.9 (3)	122.0 (7)
C63—C64—C65	117.5 (3)	117.3 (7)
C64—C65—C66	122.0 (3)	122.1 (7)
C65—C66—C61	119.3 (3)	118.9 (7)
C0—C64—C63	120.1 (3)	119.8 (7)
C0—C64—C65	122.3 (3)	122.8 (8)
O1—C1—C2	106.9 (2)	105.5 (6)
F—C2—C1	108.3 (2)	105.2 (5)
F—C2—C3	108.2 (3)	107.8 (5)
C1—C2—C3	111.3 (2)	114.1 (7)
C2—C3—C4	110.3 (3)	114.9 (7)
C3—C4—C5	110.4 (3)	116.7 (9)
C4—C5—C6	111.0 (3)	117.3 (9)
C5—C6—C1	110.5 (3)	–
O1—C1—C6	109.0 (2)	–
C2—C1—C6	111.1 (2)	–
O1—C1—C7	–	110.1 (7)
C5—C6—C7	–	125.0 (11)
C6—C7—C1	–	130.7 (9)
C7—C1—C2	–	116.6 (7)

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N-Acetyl-3,6-di-*tert*-butyl-2-(3,6-di-*tert*-butyl-3H-azepin-2-yl)-2,3-dihydro-1H-azepine

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Abstract

The deprotonation reaction of 3,6-di-*tert*-butyl-3H-azepine, (2), using methyllithium, and subsequent quenching of the resulting anionic species with acetyl