Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*92 (Sheldrick, 1992).

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Structure of 2-(1-Acetoxy-2-fluoropropyl)-*N-tert*-butylbenzenesulfonamide

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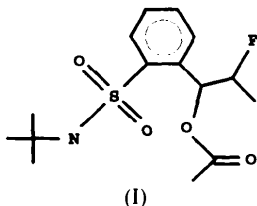*Department of Physics, Chungnam National University, Daejeon 305-764, Korea*

Abstract

The structure of the title compound, $C_{15}H_{22}FNO_4S$ [2-(*N-tert*-butylsulfamoyl)-α-(1-fluoroethyl)benzyl acetate], has been determined from a single-crystal X-ray diffraction study. The torsion angles C(7)—O(1)—C(10)—O(2) [2.5 (3)°] and C(1)—S—N—H(N) [−62.6 (2)°], and an intramolecular hydrogen bond between the N atom and O(2) [2.979 (4) Å] stabilize the structure. The structure analysis confirms opposite configurations at C(7) and C(8). The absence of close contacts less than 3.269 (4) Å [C(11)···F] shows that the molecules are bound by van der Waals forces.

Comment

Sulfonamides have long been known in organic chemistry and have found extensive use in industrial and agricultural chemistry (March, 1985). Since the discovery (Levitt, 1977) of 2-substituted sulfonamide derivatives as highly active sulfonylurea herbicides having a low use rate, high degree of selectivity and excellent environmental safety, a number of sulfonamide compounds with 2-substituents have been widely investigated (Levitt, 1991). To date, the various known sulfonamide substituents are of relatively simple type and those with chiral centers have not been reported at all. In our research program, we have synthesized the title compound (I), which was an intermediate in the synthesis of a new herbicide (Kim, 1992), but faced some difficulties in clarifying the relative configuration of two chiral centers with

NMR spectroscopy (Kitazume & Nakayama, 1986). Thus we utilized X-ray crystallography to determine the relative configuration of the diastereomers.

(I)

The final positional and equivalent isotropic thermal parameters are given in Table 1. Bond lengths, bond angles and torsion angles are listed in Table 2. An *ORTEP*II (Johnson, 1971) drawing of the molecule with the numbering of atoms is presented in Fig. 1.

A slightly distorted tetrahedral geometry is observed about the S atom. The angle O(3)—S—O(4) [118.5 (1)°] is slightly larger than the ideal tetrahedral value, while the other values are close to 109°. The two bond distances S—O(3) and S—O(4) of 1.428 (2) and 1.423 (2) Å, respectively, are comparable to the values reported in sulfones and other thio-oxides (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976; Bandoli & Nicolini, 1977; Desiraju & Kamala, 1983). The distance C(1)—S [1.779 (3) Å] is in agreement with the value quoted for a $C(sp^3)$—S single bond (1.8 Å) (Khan, Taylor, Lehn & Dietrich, 1988, and references therein). The distance S—N is 1.610 (3) Å. This value agrees with that found by Germain, Declercq, Castresana, Elizalde & Arrieta (1983) in the structure of 4-methyl-*N*-(8-quinolyl)benzenesulfonamide. The relative configuration of two chiral centers, C(7) and C(8), is not determined by NMR spectroscopy. The structure analysis confirms opposite configurations at C(7) and C(8).
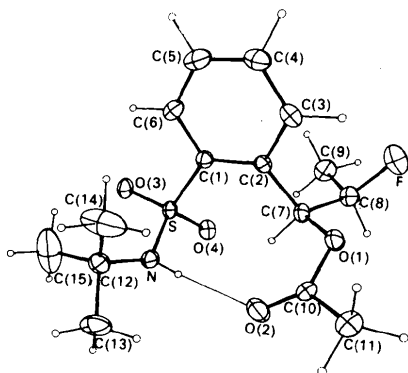
As shown in Table 2, the torsion angles N—S—C(1)—C(6), N—S—C(1)—C(2) and C(2)—C(7)—C(8)—F are −105.0 (3), 71.4 (2) and 66.0 (3)°, respectively. Also, those of C(7)—O(1)—C(10)—O(2) and C(1)—S—N—H(N) are 2.5 (3) and −62.6 (2)°, respectively. An intramolecular hydrogen bond N—H···O(2) is observed [N—H(N) 0.81 (3), N···O(2) 2.979 (4), H(N)···O(2) 2.17 (29) Å and N—H(N)···O(2) 171.9 (2)°]. Therefore, the molecular structure contains a nine-membered ring in the crystalline state.

In this molecule, the benzene ring is planar within 0.029 Å, with a maximum deviation of −0.017 (3) Å for the C(5) atom. The neighbouring atoms, S and C(7), deviate by 0.163 (5) and −0.132 (5) Å, respectively, from the best plane of benzene. Since there are no close contacts less than 3.269 (4) Å, [C(11)···F] the molecules are bound by intermolecular van der Waals forces.

Experimental

Crystal data

$C_{15}H_{22}FNO_4S$	$D_m = 1.3$ Mg m^{-3}
$M_r = 331.4$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71069$ Å
$P2_1/a$	Cell parameters from 25
$a = 13.693\ (6)$ Å	reflections
$b = 14.731\ (15)$ Å	$\theta = 10{-}15°$
$c = 8.737\ (5)$ Å	$\mu = 1.74$ mm^{-1}
$\beta = 106.51\ (5)°$	$T = 299$ K
$V = 1690\ (1)$ Å^3	Needle
$Z = 4$	$0.3 \times 0.2 \times 0.2$ mm
$D_x = 1.303$ Mg m^{-3}	Colourless

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 24°$
diffractometer	$h = -15 \rightarrow 15$
$\omega/2\theta$ scans	$k = 0 \rightarrow 16$
Absorption correction:	$l = 0 \rightarrow 9$
none	3 standard reflections
2549 measured reflections	monitored every 100
2549 independent reflections	reflections
2337 observed reflections	intensity variation: none
$[F > 3\sigma(F)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.076$
$R = 0.0598$	$\Delta\rho_{max} = 0.481$ e Å^{-3}
$wR = 0.0670$	$\Delta\rho_{min} = -0.349$ e Å^{-3}
$S = 3.5233$	Atomic scattering factors
2337 reflections	from *International Tables*
224 parameters	*for X-ray Crystallography*
Only H-atom U's refined	(1974, Vol. IV)
$w = 1/[\sigma^2(F) + 0.00034F^2]$	

Fig. 1. *ORTEP*II (Johnson, 1971) drawing and numbering scheme. The ellipsoids are drawn at the 20% probability level and H atoms are represented as spheres of arbitrary radii. The thin line indicates the intramolecular hydrogen bond.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

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

	x	y	z	U_{eq}
S	0.2176 (1)	0.3425	0.7251 (1)	0.040
F	0.0756 (2)	0.6606 (1)	0.8577 (3)	0.083
O(1)	0.2426 (2)	0.6366 (1)	0.7567 (3)	0.052
O(2)	0.3216 (2)	0.5628 (2)	0.6045 (4)	0.083
O(3)	0.2209 (2)	0.2488 (1)	0.7683 (3)	0.058
O(4)	0.1302 (1)	0.3754 (1)	0.6074 (2)	0.051
N	0.3128 (2)	0.3635 (2)	0.6569 (3)	0.045
C(1)	0.2312 (2)	0.4071 (2)	0.9020 (3)	0.039
C(2)	0.2183 (2)	0.5022 (2)	0.9026 (3)	0.037
C(3)	0.2415 (2)	0.5461 (2)	1.0485 (4)	0.052
C(4)	0.2731 (3)	0.4985 (3)	1.1913 (4)	0.061
C(5)	0.2813 (3)	0.4053 (3)	1.1883 (4)	0.067
C(6)	0.2616 (2)	0.3593 (2)	1.0443 (4)	0.053
C(7)	0.1759 (2)	0.5586 (2)	0.7527 (3)	0.043
C(8)	0.0707 (2)	0.5970 (2)	0.7359 (4)	0.052
C(9)	−0.0067 (2)	0.5269 (3)	0.7416 (5)	0.066
C(10)	0.3137 (3)	0.6290 (2)	0.6793 (4)	0.050
C(11)	0.3779 (3)	0.7120 (2)	0.6950 (5)	0.070
C(12)	0.4207 (2)	0.3314 (2)	0.7215 (4)	0.057
C(13)	0.4770 (3)	0.3671 (4)	0.6105 (5)	0.097
C(14)	0.4689 (4)	0.3677 (6)	0.8839 (6)	0.162
C(15)	0.4217 (5)	0.2279 (4)	0.7187 (12)	0.191

Table 2. Geometric parameters (Å, °)

C(1)—C(2)	1.412 (4)	C(1)—C(6)	1.386 (4)
C(1)—S	1.779 (3)	C(2)—C(3)	1.383 (4)
C(2)—C(7)	1.520 (4)	C(3)—C(4)	1.389 (5)
C(4)—C(5)	1.378 (6)	C(5)—C(6)	1.386 (5)
C(7)—C(8)	1.515 (4)	C(7)—O(1)	1.462 (3)
C(8)—C(9)	1.491 (5)	C(8)—F	1.405 (4)
C(10)—C(11)	1.489 (5)	C(10)—O(1)	1.339 (5)
C(10)—O(2)	1.196 (4)	C(12)—C(13)	1.495 (5)
C(12)—C(14)	1.484 (7)	C(12)—C(15)	1.525 (7)
C(12)—N	1.500 (4)	O(3)—S	1.428 (2)
O(4)—S	1.423 (2)	S—N	1.610 (3)
C(3)—C(2)—C(1)	118.1 (2)	C(4)—C(3)—C(2)	121.5 (3)
C(5)—C(4)—C(3)	119.5 (3)	C(5)—C(6)—C(1)	119.8 (3)
C(6)—C(1)—C(2)	120.4 (2)	C(6)—C(5)—C(4)	120.6 (3)
C(7)—C(2)—C(1)	123.8 (2)	C(7)—C(2)—C(3)	118.0 (3)
C(8)—C(7)—C(2)	114.0 (2)	C(9)—C(8)—C(7)	113.8 (3)
C(10)—O(1)—C(7)	117.5 (2)	C(14)—C(12)—C(13)	108.8 (3)
C(15)—C(12)—C(13)	109.4 (4)	C(15)—C(12)—C(14)	111.8 (5)
F—C(8)—C(7)	109.6 (2)	F—C(8)—C(9)	108.5 (3)
O(1)—C(7)—C(2)	109.0 (2)	O(1)—C(7)—C(8)	106.2 (2)
O(1)—C(10)—C(11)	112.3 (3)	O(2)—C(10)—C(11)	125.3 (4)
O(2)—C(10)—O(1)	122.4 (3)	O(3)—S—C(1)	107.4 (1)
O(4)—S—C(1)	107.7 (1)	O(4)—S—O(3)	118.5 (1)
S—C(1)—C(2)	123.5 (2)	S—C(1)—C(6)	116.0 (2)
S—N—C(12)	127.9 (2)	N—C(12)—C(13)	106.2 (3)
N—C(12)—C(14)	111.7 (3)	N—C(12)—C(15)	108.8 (3)
N—S—C(1)	108.8 (1)	N—S—O(3)	108.4 (2)
N—S—O(4)	105.7 (1)		

C(6)—C(1)—C(2)—C(3)	3.0 (3)
S—C(1)—C(2)—C(3)	−173.2 (4)
C(2)—C(1)—C(6)—C(5)	−1.2 (3)
C(2)—C(1)—S—O(3)	−171.5 (3)
C(2)—C(1)—S—N	71.4 (2)
C(6)—C(1)—S—O(4)	140.9 (2)
C(1)—C(2)—C(3)—C(4)	−2.3 (3)
C(1)—C(2)—C(7)—C(8)	110.0 (3)
C(3)—C(2)—C(7)—C(8)	−67.1 (3)
C(2)—C(3)—C(4)—C(5)	−0.3 (3)
C(4)—C(5)—C(6)—C(1)	−1.4 (3)
C(2)—C(7)—C(8)—F	66.0 (3)
O(1)—C(7)—C(8)—F	−54.0 (2)
C(8)—C(7)—O(1)—C(10)	−140.9 (3)
O(2)—C(10)—O(1)—C(7)	2.5 (3)
C(14)—C(12)—N—S	−63.7 (4)
C(1)—S—N—C(12)	74.0 (3)

O(4)—S—N—C(12)	−170.5 (3)
C(6)—C(1)—C(2)—C(7)	−174.1 (4)
S—C(1)—C(2)—C(7)	9.7 (2)
S—C(1)—C(6)—C(5)	175.3 (4)
C(2)—C(1)—S—O(4)	−42.7 (2)
C(6)—C(1)—S—O(3)	12.2 (2)
C(6)—C(1)—S—N	−105.0 (3)
C(7)—C(2)—C(3)—C(4)	175.0 (4)
C(1)—C(2)—C(7)—O(1)	−131.5 (3)
C(3)—C(2)—C(7)—O(1)	51.4 (3)
C(3)—C(4)—C(5)—C(6)	2.2 (3)
C(2)—C(7)—C(8)—C(9)	−55.7 (3)
O(1)—C(7)—C(8)—C(9)	−175.8 (3)
C(2)—C(7)—O(1)—C(10)	95.8 (3)
C(11)—C(10)—O(1)—C(7)	−178.8 (4)
C(13)—C(12)—N—S	177.8 (4)
C(15)—C(12)—N—S	60.1 (4)
O(3)—S—N—C(12)	−42.5 (3)

Space group and approximate cell dimensions of this crystal were determined by preliminary experiment using Weissenberg and precession photography (Suh, Suh, Ko, Aoki & Yamazaki, 1988; Suh, Suh, Ko, Aoki & Yamazaki, 1989; Suh, Suh & Ko, 1989). The structure was solved by direct methods with *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Refinement was by full-matrix least squares (*SHELX*76; Sheldrick, 1976), with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms. H-atom positions except H(N) were fixed geometrically (C—H = 1.08 Å) and not refined. Geometric calculations on the crystal and molecular structure were performed using *GEOM* (Shin, 1978). All computations were performed using MicroVAX 3400 and PC 486 computers.

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$C_{15}H_{22}FNO_4S$

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An Octahydro-3a,6-methanoazulen-5-one Resulting from an Intramolecular Friedel–Crafts Acylation

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ASHFAQUZZAMAN SYED†

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Abstract
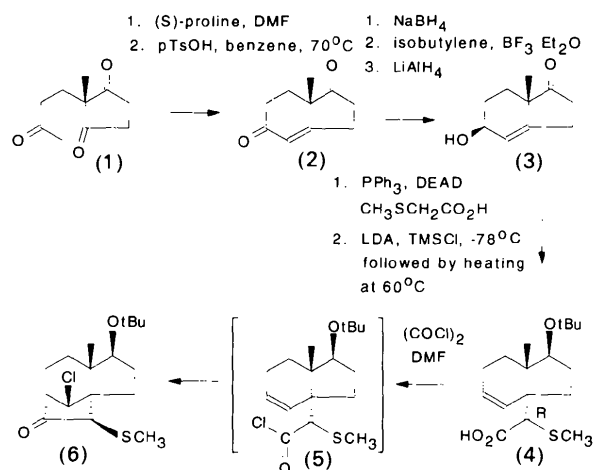
The compound (1*S*,3a*R*,4*R*,6*S*,8a*S*,9*S*)-1-*tert*-butoxy-9-chloro-2,3,3a,4,6,7,8,8a-octahydro-8a-methyl-4-methylthio-1*H*-3a,6-methanoazulen-5-one, $C_{17}H_{27}ClO_2S$, was identified as the reaction product when the acid chloride formed from a *trans*-fused perhydroindane derivative underwent a Friedel–Crafts acylation of the internal olefin.

Comment

As part of a program to synthesize the *C* and *D* rings of the cucurbitanes (see Richardson, Sabol & Watt, 1989), the proline-catalyzed cyclization of the prochiral

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triketone (1) was employed to secure the enone (2) in high enantiomeric excess and good yield (see Hajos & Parrish, 1974). Successive reduction and protection of the non-conjugated carbonyl in (2) was followed by reduction of the conjugated carbonyl to afford the allylic alcohol (3). A Mitsunobu inversion with (methylthio)acetic acid set the stage for a Claisen rearrangement that led

to the substituted *trans*-fused perhydroindane skeleton in the intermediate carboxylic acid (4) (Richardson *et al.*, 1989). At this stage, the carboxylic acid functionality in (4) was superfluous and methods for removing this one-carbon unit were investigated. In order to achieve the decarboxylation of (4), derivatives of the carboxylic acid (*e.g.* the phenylseleno ester) were examined. Preparation of the esters required the activation of the carboxylic acid as the acid chloride but the intermediate acid chloride (5)
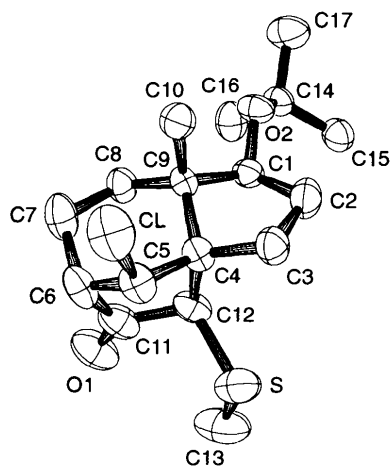

Fig. 1. Perspective drawing of the molecular structure of TRICYC showing the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms have been omitted for clarity.