

The Crystal and Molecular Structure of N-*tert*-Butyl-2-(1-acetoxy-2-fluoro-1-butyl)benzenesulfonamide, C₁₆H₂₄FNO₄S

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N-*tert*-Butyl-2-(1-acetoxy-2-fluoro-1-butyl)benzenesulfonamide의 결정 및 분자구조

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Abstract

The structure of N-*tert*-Butyl-2-(1-acetoxy-2-fluoro-1-butyl)benzenesulfonamide (C₁₆H₂₄FNO₄S) has been determined by X-ray diffraction methods. The crystals are monoclinic, space group *P2₁/c*, unit cell constants $a=8.583(2)$ Å, $b=14.674(2)$ Å, $c=14.703(2)$ Å, $\beta=103.23(1)^\circ$, $Z=4$, $V=1802.6(5)$ Å³, $D_c=1.27$ Mg m⁻³. The intensity data were collected on a Rigaku AFC-5 Diffractometer with a graphite monochromated Cu-K α radiation. The structure was solved by direct method and refined by full-matrix least-square calculations to a final R value of 0.069 for 2472 observed reflections. There is an intramolecular hydrogen bond between the N(7) atom and O(4) [2.990(4) Å]. The structure analysis confirms opposite configurations at C(14) and C(15). The absence of close contacts less than 3.465(5) Å [C(19)⋯O(5)] (symmetry code: $-x, y+1/2, -z+1/2$) show that the molecules are bound by van der Waals forces.

요 약

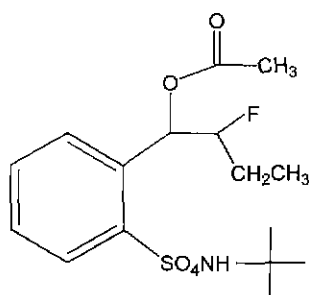
N-*tert*-Butyl-2-(1-acetoxy-2-fluoro-1-butyl)benzenesulfonamide의 분자 및 결정구조를 X-선회절법으로 연구하였다. 결정의 공간군은 *P2₁/c*이고, 단위포 상수는 $a=8.583(2)$ Å, $b=14.674(2)$ Å, $c=14.703(2)$ Å, $\beta=103.23(1)^\circ$, $Z=4$, $V=1802.6(5)$ Å³, $D_c=1.27$ Mg m⁻³이다. 회절반점들의 세기는 Rigaku AFC-5 Diffractometer로 얻었으며, graphite로 단색화한 Cu-K α X-선을 사용하였다. 분자구조는 직접법으로 풀었으며 최소자승법으로 정밀화하였다. 최종신뢰도 R값은 2472개의 회절반점에 대하여 0.069였다. 분자 내에 N(7)과 O(4) 사이에 1개의 수소결합[2.990(4) Å]을 갖고 있으며, C(14)와 C(15)는 반대배열을 갖고 있다. 분자간 가장 인접한 거리는 3.465(5) Å [C(19)⋯O(5)] (symmetry code: $-x, y+1/2, -z+1/2$)로 분자간 접촉은 van der Waals 힘에 의해 결합되어 있다.

1. Introduction

Sulfonamides have long been known in organic chemistry and have found extensive use in industrial and agricultural chemistry.¹⁾ Since the

discovery²⁾ 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.¹⁰⁾ 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,⁷⁾ but faced some difficulties in clarifying the relative configuration of two chiral centers with NMR spectroscopy.⁸⁾ Thus we utilized X-ray crystallography to determine the relative configuration of the diastereomers.



(I)

2. Experiment

Space group and approximate cell dimension of this crystal were determined by preliminary experiment using Weissenberg and precession photography.¹⁵⁻¹⁷⁾

The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic thermal factors for all the non-H atoms. All H-atom positions except for the H(7) were fixed geometrically (C-H=1.08 Å) and the H(7) atom was found in the difference electron-density maps calculated at the end refinement process and they were not refined. Geometric calculations on the crystal and molecular structure were performed using GEOM.¹⁴⁾ All computations were performed using SUN SPARC station IPC and PC586 computers.

Experimental details are listed in Table 1.

Data collection, cell refinement and data reduction: XDC (Rigaku). Program used to solve

Table 1. Crystal data and structure refinement for $rm\ C_{16}H_{24}FNO_4S$

Crystal data	
$C_{16}H_{24}FNO_4S$	CuK α radiation
$M_r=345.42$	$\lambda=1.5418\ \text{\AA}$
Monoclinic	Cell parameters
$P2_1/c$	from 20
$a=8.583(2)\ \text{\AA}$	reflections
$b=14.674(2)\ \text{\AA}$	$\theta=17.5^\circ-32.5^\circ$
$c=14.703(2)\ \text{\AA}$	$\mu=1.844\ \text{mm}^{-1}$
$\beta=103.23(1)^\circ$	$T=293(2)\text{K}$
$V=1802.6(5)\ \text{\AA}^3$	Needle
$Z=4$	$0.3\times 0.3\times 0.2\ \text{mm}$
$D_x=1.273\ \text{Mg m}^{-3}$	Colorless
D_m not measured	Synthesis
Data collection	
Rigaku AFC-5 diffractometer	$\theta_{\text{max}}=62.60^\circ$
$\omega/2\theta$ scans	$h=-9 \rightarrow 9$
Absorption correction: ψ scan	$k=0 \rightarrow 15$
$T_{\text{min}}=0.98, T_{\text{max}}=1.00$	$l=-16 \rightarrow 0$
3003 measured reflections	4 standard reflections
2879 independent reflections	every 100
2472 observed reflections	reflections
$>2\sigma(I)$	intensity
$R_{\text{int}}=0.1221$	decay: none
Refinement	
Refinement on F^2	$(\Delta/\sigma)_{\text{max}}=0.000$
$R[F^2>2\sigma(F^2)]=0.0690$	$\Delta\rho_{\text{max}}=0.639\ \text{e}\text{\AA}^{-3}$
$wR(F^2)=0.2106$	$\Delta\rho_{\text{min}}=-0.550\ \text{e}\text{\AA}^{-3}$
$S=1.090$	Extinction correction:
2879 reflections	SHELXL
209 parameters	Extinction coefficient:
mixed	0.007(1)
$w=1/[\sigma^2(F_o^2)+(0.1183P)^2$	Scattering factors
$+2.0329P]$	from <i>international</i>
where $P=(F_o^2+2F_c^2)/3$	Tables for
	Crystallography
	(Vol. C)

structure: SHELXS86.¹²⁾ Program used to refine structure: SHELXL97.¹³⁾ Molecular graphics: ORTEP III.⁵⁾

3. Discussion

The final positional and equivalent isotropic

thermal parameters are given in Table 2 and Table 3. Bond lengths, bond angles and torsion angles are listed in Table 4. An ORTEP III⁵⁾ drawing of the molecule with the numbering and packing of atoms are presented in Fig. 1 and Fig. 2.

A slightly distorted tetrahedral geometry is observed about the S(1) atom. The angle O(5)-S(1)-O(6) [118.2(2)°] is slightly larger than the ideal tetrahedral value, while the other values are close to 109°. The two bond distances S(1)-O(5) and S(1)-O(6) of 1.430(3) and 1.426(3) Å, respectively, are comparable to the values reported in sulfones and other thio-oxides.¹⁻³⁾ The distance C(13)-S(1) [1.780(4) Å] is in agreement with the value quoted for a C(sp³)-S

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for non-hydrogen atoms of *rm* C₁₆H₂₄FNO₄S. The e.s.d.'s are in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
S(1)	0.7303(1)	0.1712(1)	0.2556(1)	0.044(1)
F(2)	0.8846(4)	-0.1315(2)	0.1020(2)	0.082(1)
O(3)	0.7739(3)	-0.1256(2)	0.2598(2)	0.056(1)
O(4)	0.6271(6)	-0.0604(2)	0.3473(3)	0.093(1)
O(5)	0.6150(3)	0.1404(2)	0.1752(2)	0.059(1)
O(6)	0.7690(4)	0.2658(2)	0.2626(2)	0.064(1)
N(7)	0.6634(4)	0.1422(2)	0.3446(2)	0.047(1)
C(8)	0.9160(4)	0.0152(2)	0.2455(2)	0.042(1)
C(9)	1.0653(5)	-0.0260(3)	0.2635(3)	0.053(1)
C(10)	1.2049(5)	0.0233(4)	0.2925(3)	0.063(1)
C(11)	1.1973(5)	0.1155(4)	0.3028(3)	0.065(1)
C(12)	1.0522(5)	0.1588(3)	0.2885(3)	0.056(1)
C(13)	0.9107(4)	0.1094(2)	0.2609(2)	0.042(1)
C(14)	0.7690(5)	-0.0424(2)	0.2051(3)	0.045(1)
C(15)	0.7582(5)	-0.0727(3)	0.1051(3)	0.054(1)
C(16)	0.7571(6)	0.0033(3)	0.0379(3)	0.059(1)
C(17)	0.7409(7)	-0.0279(4)	-0.0620(3)	0.080(2)
C(18)	0.6978(5)	-0.1251(3)	0.3289(3)	0.053(1)
C(19)	0.7114(6)	-0.2139(3)	0.3784(3)	0.068(1)
C(20)	0.7169(6)	0.1725(3)	0.4427(3)	0.070(1)
C(21)	0.6169(8)	0.1262(5)	0.4986(4)	0.104(2)
C(22)	0.6830(3)	0.2698(5)	0.4465(7)	0.082(1)
C(23)	0.8808(9)	0.1496(14)	0.4809(5)	0.093(1)

single bond (1.8 Å).⁶⁾ The distance S(1)-N(7) is 1.603(3) Å. This value agrees with that found by Germain, Declercq, Castresana, Elizalde &

Table 3. Fractional atomic coordinates for hydrogen atoms of *rm* C₁₆H₂₄FNO₄S

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(7)	0.5857	0.1038	0.3339
H(9)	1.0716	-0.0887	0.2557
H(10)	1.3034	-0.0062	0.3050
H(11)	1.2912	0.1492	0.3197
H(12)	1.0483	0.2215	0.2971
H(14)	0.6726	-0.0078	0.2079
H(15)	0.6583	-0.1069	0.0844
H(16A)	0.8556	0.0377	0.0572
H(16B)	0.6690	0.0439	0.0403
H(17A)	0.7410	0.0242	-0.1015
H(17B)	0.6422	-0.0607	-0.0824
H(17C)	0.8290	-0.0669	-0.0655
H(19A)	0.7742	-0.2551	0.3507
H(19B)	0.6065	-0.2391	0.3735
H(19C)	0.7623	-0.2050	0.4431
H(21A)	0.5063	0.1409	0.4738
H(21B)	0.6481	0.1462	0.5624
H(21C)	0.6314	0.0614	0.4959
H(22A)	0.5717	0.2806	0.419
H(22B)	0.7465	0.3030	0.4117
H(22C)	0.7089	0.2899	0.5103
H(23A)	0.8949	0.0850	0.4764
H(23B)	0.9099	0.1676	0.5453
H(23C)	0.9475	0.1807	0.4467

Table 4. Bond lengths, angles, selected torsion angles and hydrogen bond with e.s.d.s in parentheses

(1) Bond lengths (Å)			
S(1)-O(6)	1.426(3)	C(9)-C(10)	1.381(6)
S(1)-O(5)	1.430(3)	C(10)-C(11)	1.366(7)
S(1)-N(7)	1.603(3)	C(11)-C(12)	1.370(6)
S(1)-C(13)	1.780(4)	C(12)-C(13)	1.393(5)
F(2)-C(15)	1.395(5)	C(14)-C(15)	1.517(5)
O(3)-C(18)	1.328(5)	C(15)-C(16)	1.489(6)
O(3)-C(14)	1.457(4)	C(16)-C(17)	1.513(6)
O(4)-C(18)	1.191(5)	C(18)-C(19)	1.483(6)
N(7)-C(20)	1.478(5)	C(20)-C(23)	1.430(11)
C(8)-C(9)	1.386(5)	C(20)-C(22)	1.462(10)
C(8)-C(13)	1.403(5)	C(20)-C(21)	1.482(7)
C(8)-C(14)	1.522(5)		

Table 4. Continued

(2) Bond angles (°)			
O(6)-S(1)-O(5)	118.24(18)	C(8)-C(13)-S(1)	123.7(3)
O(6)-S(1)-N(7)	108.70(17)	O(3)-C(14)-C(15)	106.1(3)
O(5)-S(1)-N(7)	106.35(18)	O(3)-C(14)-C(8)	109.5(3)
O(6)-S(1)-C(13)	107.88(18)	C(15)-C(14)-C(8)	113.7(3)
O(5)-S(1)-C(13)	107.81(16)	F(2)-C(15)-C(16)	109.1(4)
N(7)-S(1)-C(13)	107.41(16)	F(2)-C(15)-C(14)	109.7(3)
C(18)-O(3)-C(14)	117.5(3)	C(16)-C(15)-C(14)	114.4(3)
C(20)-N(7)-S(1)	128.9(3)	C(15)-C(16)-C(17)	113.8(4)
C(9)-C(8)-C(13)	117.5(4)	O(4)-C(18)-O(3)	122.9(4)
C(9)-C(8)-C(14)	118.6(3)	O(4)-C(18)-C(19)	125.1(4)
C(13)-C(8)-C(14)	123.7(3)	O(3)-C(18)-C(19)	112.0(4)
C(10)-C(9)-C(8)	122.0(4)	C(23)-C(20)-C(22)	113.6(11)
C(11)-C(10)-C(9)	119.6(4)	C(23)-C(20)-N(7)	111.8(6)
C(10)-C(11)-C(12)	120.5(4)	C(22)-C(20)-N(7)	108.1(6)
C(11)-C(12)-C(13)	120.3(4)	C(23)-C(20)-C(21)	108.5(7)
C(12)-C(13)-C(8)	120.1(4)	C(22)-C(20)-C(21)	106.4(8)
C(12)-C(13)-S(1)	116.0(3)	N(7)-C(20)-C(21)	108.3(4)

(3) Selected torsion angles (°)

N(7)-S(1)-C(13)-C(8)	70.5(3)
N(7)-S(1)-C(13)-C(12)	-104.9(3)
C(8)-C(13)-S(1)-O(5)	-43.8(3)
C(8)-C(13)-S(1)-O(6)	-172.5(3)
C(8)-C(13)-S(1)-N(7)	70.5(3)
C(8)-C(14)-O(3)-C(18)	93.7(4)
C(8)-C(14)-C(15)-F(2)	65.3(4)
C(8)-C(14)-C(15)-C(16)	-57.8(4)
C(13)-S(1)-N(7)-H(7)	-101.7(2)
C(13)-S(1)-N(7)-C(20)	78.3(4)
C(13)-C(8)-C(14)-O(3)	-134.5(4)

Table 4. Continued

C(13)-C(8)-C(14)-C(15)	107.1(4)
C(14)-O(3)-C(18)-O(4)	.0(4)
C(14)-O(3)-C(18)-C(19)	179.7(5)
C(14)-C(15)-C(16)-C(17)	-178.1(6)

(4) Hydrogen-bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N(7)-H(7)...O(4)	0.86(3)	2.43(3)	2.990(4)	122.7(26)

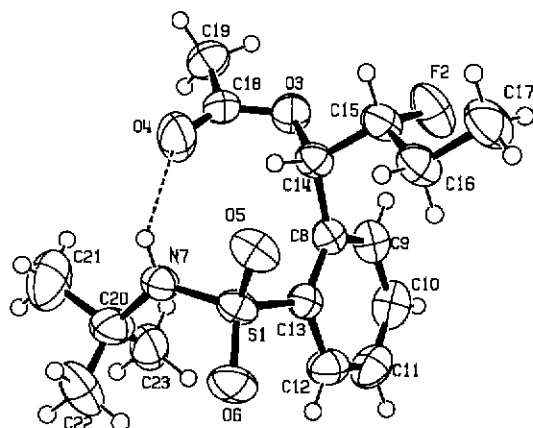


Fig. 1. An ORTEP (III) drawing of NBB with the atomic numbering scheme. The displacement ellipsoids are drawn on the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

Arrieta (1983) in the structure of 4-methyl-*N*-(8-quinolyl)benzenesulfonamide.

The relative configuration of two chiral centers,

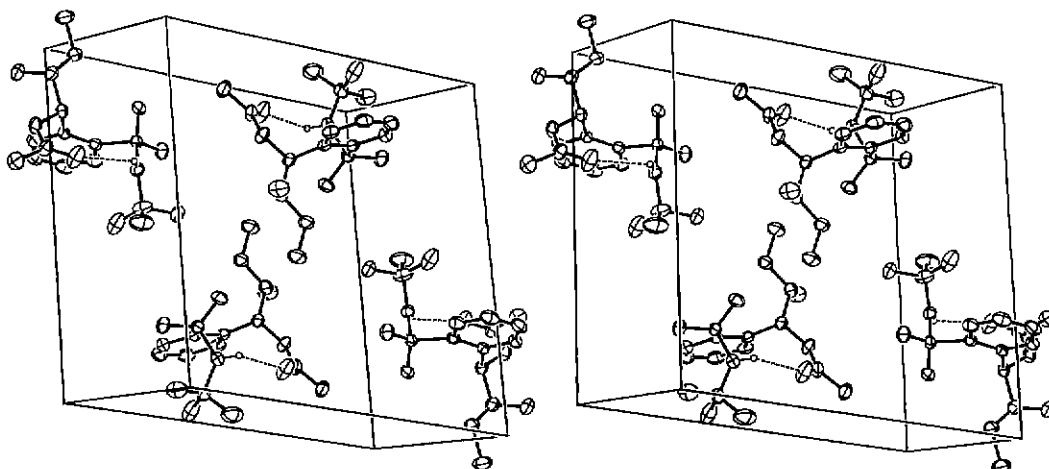


Fig. 2. A stereoscopic view of the packing for NBB. The c-axis is vertical and b-axis horizontal.

C(14) and C(15), is not determined by NMR spectroscopy. The structure analysis confirms opposite configurations at C(14) and C(15). As shown in Table 3, the torsion angles N(7)-S(1)-C(13)-C(12), N(7)-S(1)-C(13)-C(8) and C(8)-C(14)-C(15)-F(2) are $-104.9(3)$, $70.5(3)$ and $65.3(4)^\circ$, respectively. Also, those of C(14)-O(3)-C(18)-O(4) and C(13)-S(1)-N(7)-H(7) are $0.0(4)$ and $-101.7(2)^\circ$, respectively. An intramolecular hydrogen bond N(7)-H(7) \cdots O(4) is observed [N(7)-H(7) $0.86(3)$, N(7) \cdots O(4) $2.990(4)$, H(7) \cdots O(4) $2.437(30)$ Å and N(7)-H(N(7)) \cdots O(4) $122.7(2)^\circ$]. Therefore, the molecular structure contains a nine-membered ring in the crystalline state.

In this molecule, the benzene ring is planar within 0.034 Å, with a maximum deviation of $-0.018(4)$ Å for the C(8) atom. The neighbouring atoms, S(1) and C(14), deviate by $0.202(6)$ and $-0.160(6)$ Å, respectively, from the best plane of benzene. Since there are no close contacts less than $3.468(5)$ Å, [C(19) \cdots O(5)] the molecules are bound by intermolecular van der Waals forces.

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