Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3808 measured reflections
3392 independent reflections
1805 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.02$
$\theta_{\rm max} = 26.3°$
$h = -10 \rightarrow 9$
$k = -12 \rightarrow 0$
$l = -14 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 0.2%

Refinement

Refinement on F
$R = 0.0401$
$wR = 0.0419$
$S = 1.26$
1805 reflections
217 parameters
H atoms: see below
$w = 1/[\sigma^2(F^2) + (0.04F^2)^2]$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.241$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.116$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C9	1.216 (4)	C1—C12	1.490 (3)
O2—C9	1.359 (3)	C2—C3	1.379 (4)
O2—C10	1.433 (4)	C2—C9	1.469 (5)
O3—C12	1.210 (3)	C3—C4	1.512 (5)
O4—C12	1.341 (3)	C4—C5	1.526 (4)
O4—C13	1.447 (3)	C5—C6	1.518 (4)
O5—C16	1.425 (3)	C6—C7	1.532 (5)
O5—C17	1.409 (5)	C7—C8	1.496 (4)
N1—C3	1.359 (4)	C10—C11	1.481 (4)
N1—C15	1.451 (5)	C13—C14	1.482 (4)
N1—C18	1.459 (3)	C15—C16	1.500 (4)
C1—C2	1.471 (4)	C17—C18	1.503 (4)
C1—C8	1.336 (5)		
C9—O2—C10	116.5 (2)	C4—C5—C6	114.1 (2)
C12—O4—C13	116.6 (2)	C5—C6—C7	114.2 (3)
C16—O5—C17	108.8 (3)	C6—C7—C8	114.4 (2)
C3—N1—C15	123.4 (2)	C1—C8—C7	127.3 (3)
C3—N1—C18	123.8 (3)	O1—C9—O2	121.8 (3)
C15—N1—C18	112.1 (3)	O1—C9—C2	127.0 (3)
C2—C1—C8	124.3 (2)	O2—C9—C2	111.1 (3)
C2—C1—C12	116.3 (3)	O2—C10—C11	107.0 (3)
C8—C1—C12	119.3 (3)	O3—C12—O4	122.7 (2)
C1—C2—C3	121.0 (3)	O3—C12—C1	124.5 (2)
C1—C2—C9	116.5 (2)	O4—C12—C1	112.8 (2)
C3—C2—C9	122.4 (3)	O4—C13—C14	107.2 (2)
N1—C3—C2	123.5 (3)	N1—C15—C16	111.0 (3)
N1—C3—C4	116.6 (2)	O5—C16—C15	112.5 (2)
C2—C3—C4	119.9 (3)	O5—C17—C18	112.0 (3)
C3—C4—C5	115.0 (2)	N1—C18—C17	111.3 (2)

All H atoms were geometrically located 0.95 Å from their parent atoms and included using a riding model; displacement parameters were fixed at $1.3U_{\rm eq}$ of the parent atom.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1416). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Amino-6-fluorobenzothiazole

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Abstract

Crystals of 2-amino-6-fluoro-1,3-benzothiazole, $C_7H_5FN_2S$, have an amphiphilic layer-like structure. Each amino substituent donates two protons to hydrogen bonds and accepts one. The ring N atoms accept one proton. The F atoms are not involved in any hydrogen bonds.

Comment

We have been interested in the possibility that covalently bound F atoms might act as hydrogen-bond acceptors. The structure determination of the title compound, (I), was undertaken because it is an uncharged fluorinated organic molecule having hydrogen-bond donors.

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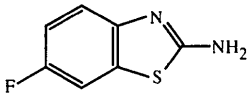
† Deceased.



(I)

Both H atoms of the amino substituent of (I) (Fig. 1) participate in N—H···N hydrogen bonds; the F atoms do not act as acceptors (see Fig. 2). Pairs of molecules form hydrogen-bonded dimers around inversion centers [N2···N3($1-x$, $1-y$, $-z$) 2.982 (2) Å]. Dimers are stacked along **b**; adjacent stacks are related by *c*-glide planes (or 2_1 screw axes) to give the familiar herringbone packing pattern of flat organic molecules. There are also chains of weaker N—H···N bonds along the 2_1 axes [N2···N2($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) 3.246 (2) Å].

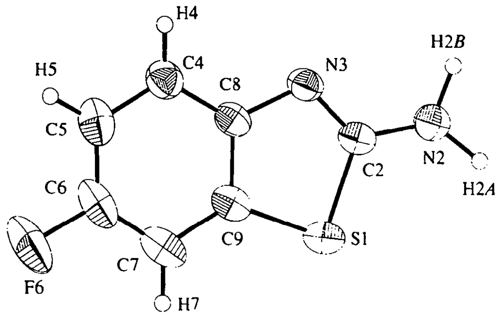


Fig. 1. *ZORTEP* (Zsolnai, 1995) plot at 50% probability of 2-amino-6-fluorobenzothiazole.

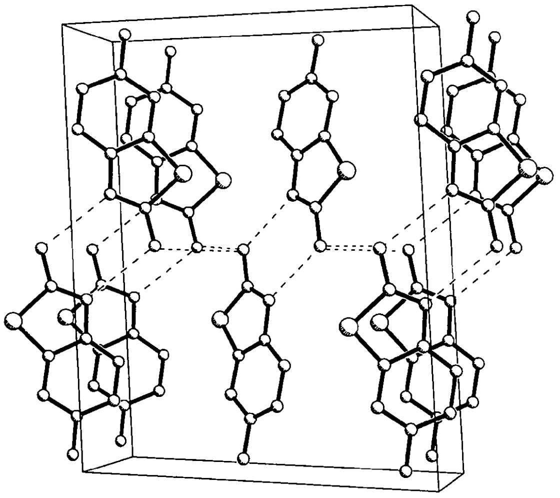


Fig. 2. The packing of 2-amino-6-fluorobenzothiazole. The structure forms alternating hydrophobic and hydrophilic layers.

The structure can be viewed as being composed of amphiphilic molecules. Molecules are related by hydrophilic interactions around $x = \frac{1}{2}$ and by hydrophobic interactions around $x = 0$.

Experimental

The title compound was obtained from the Aldrich Chemical Company and recrystallized from 95% ethyl alcohol.

Crystal data

$C_7H_5FN_2S$
$M_r = 168.19$
Monoclinic
$P2_1/c$
$a = 14.861$ (3) Å
$b = 3.980$ (5) Å
$c = 11.926$ (2) Å
$\beta = 93.21$ (2)°
$V = 704.2$ (9) Å^3
$Z = 4$
$D_x = 1.586$ Mg m^{-3}
$D_m = 1.59$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.4$–20.9°
$\mu = 0.401$ mm^{-1}
$T = 293$ (2) K
Needle
0.5 × 0.2 × 0.2 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.86$, $T_{\max} = 0.92$
1692 measured reflections
1692 independent reflections
1454 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 28°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 5$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 240 min intensity decay: 0.9%

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.111$
$S = 0.93$
1692 reflections
102 parameters
H atoms: C—H calculated and N—H found on the difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 0.187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C9	1.736 (2)	C8—C9	1.407 (2)
S1—C2	1.756 (2)	C9—C7	1.386 (2)
N3—C2	1.295 (2)	F6—C6	1.358 (2)
N3—C8	1.390 (2)	C4—C5	1.382 (3)
C2—N2	1.358 (2)	C6—C7	1.375 (3)
C8—C4	1.390 (2)	C6—C5	1.381 (3)
C9—S1—C2	88.71 (8)	C7—C9—S1	128.69 (14)
C2—N3—C8	110.53 (13)	C8—C9—S1	109.44 (12)
N3—C2—N2	124.89 (15)	C5—C4—C8	119.8 (2)
N3—C2—S1	116.24 (12)	F6—C6—C7	118.1 (2)
N2—C2—S1	118.71 (12)	F6—C6—C5	117.7 (2)
C4—C8—N3	125.66 (14)	C7—C6—C5	124.2 (2)
C4—C8—C9	119.3 (2)	C4—C5—C6	118.7 (2)
N3—C8—C9	115.07 (14)	C6—C7—C9	116.2 (2)
C7—C9—C8	121.9 (2)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1995).

The help of Professor John M. Hughes, Department of Geology, Miami University, Oxford, USA, is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(*E*)-But-2-enoxy-1,2-benzisothiazole 1,1-Dioxide: Unusual C—O—C Ether Bond Lengths and Reactivity

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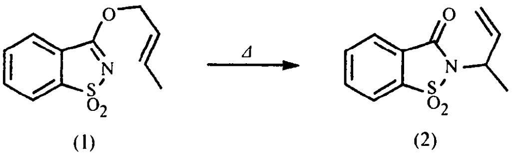
Abstract

Ethers such as the title compound, $C_{11}H_{11}NO_3S$, (1), rearrange thermally to give *N*-allyl isomers, (2), in high yield. The X-ray structure determination of the title ether shows a central C—O—C linkage which has one very short (notional) C—O single bond and one exceptionally long single C—O bond. The thermal migration of allyl from the O to the N atom involves the breaking of one of the ether bonds in (1) and a shortening of the other as it becomes a formal carbonyl group in the product (2). The rearrangement is thus considerably assisted by the ground-state structure of the starting ether, in which the bond to be broken is already stretched and the one that is to form a carbonyl group is already a substantial partial double bond.

Comment

Compounds bearing an allylic alcohol function are often vital structural units of biologically active systems. In addition, allylic alcohols have attracted widespread attention as key intermediates for the synthesis of various types of compounds (Kumar & Dittmer, 1994; Adam, Peters & Renz, 1994; Evans, Holmes & Russell, 1994; Bergmeier & Stanchina, 1995; Fujii, Habashita, Akaji, Nakai, Ibuka, Fujiwara, Tamamura & Yamamoto, 1996).

The title compound, (1), can be prepared readily from 3-chloro-1,2-benzisothiazole 1,1-dioxide (pseudosaccharyl chloride) and crotyl alcohol in the presence of base. It undergoes easy thermal rearrangement to the *N*-allyl isomer [(2); see scheme below]. Formally, this [3,3] rearrangement is similar to that reported for 5-allyloxy-1-phenyltetrazoles (Cristiano, 1994; Cristiano, Johnstone & Price, 1996). Under some conditions, [1,3] migration may also occur. Recent investigations concerning the structure and reactivity of aryloxytetrazoles and aryloxypseudosaccharins towards catalytic hydrogenolysis and cross-coupling have shown that much of the reactivity of these ethers can be ascribed to unusual bond lengths in the central C—O—C ether bonds caused by a usually powerful electronegative effect from the tetrazole or pseudosaccharyl ring system (Brigas & Johnstone, 1996; Alves, Brigas & Johnstone, 1996; Alves, 1996). For example, aryloxypseudosaccharins (3-aryloxy-1,2-benzisothiazole 1,1-dioxides) are characterized by having an ether linkage in which one C—O bond is long and the other is short. The effect of the benzisothiazole 1,1-dioxide ring system is to lengthen the aryl C—O bond from a typical value of 1.36 Å in a phenol to about 1.44 Å in the ether. At the same time, the link from the ether oxygen to the pseudosaccharyl system is very short (1.32 Å) for a C—O single bond, *viz.* it is a partial double bond. The net result of these electronic changes on converting a phenol into its pseudosaccharyl ether is to provide a molecular structure that lies close to the supposed transition-state structure for the migration shown below, in which an originally strong phenolic C—O bond becomes easily cleavable catalytically in the ether.



(1) (2)

Because of the ease of rearrangement of allyloxypseudosaccharins such as compound (1) (see scheme above), it was of interest to discover whether or not the electronegative pseudosaccharyl system was exerting a strong electronic influence on the allyloxy group,