

*Acta Cryst.* (1998). **C54**, 251–253

**Electronic Effects on C—O—C Ether Bonds in 3-Aryloxy Derivatives of Benzisothiazole 1,1-Dioxides: Rapid Ethanolysis of 3-(4-Nitrophenoxy)-1,2-benzisothiazole 1,1-Dioxide, (1), to give 3-Ethoxy-1,2-benzisothiazole 1,1-Dioxide, (2)**

AMADEU F. BRIGAS,<sup>a</sup> PEDRO M. GONCALVES<sup>a</sup> AND ROBERT A. W. JOHNSTONE<sup>b</sup>

<sup>a</sup>UCEH, Campus de Gambelas, Universidade do Algarve, 8000 Faro, Portugal, and <sup>b</sup>Department of Chemistry, University of Liverpool, Liverpool L69 3BX, England.  
E-mail: rj05@liverpool.ac.uk

(Received 8 April 1997; accepted 14 October 1997)

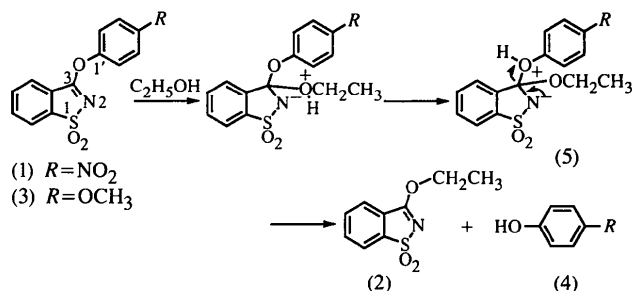
**Abstract**

The bond lengths in the central C—O—C ether linkage of title compound (1), C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>S, are comparable with those found in earlier work on similar compounds. However, (1) was found to undergo very easy solvolysis with ethanol to give (2), C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>S, for which a structure was also determined, but 3-(4-methoxyphenoxy)-1,2-benzisothiazole 1,1-dioxide, (3), did not hydrolyse under the same conditions. If ground-state structures are important for solvolysis, these results suggest that there should be a difference in the corresponding C—O bond lengths for the ethers (1) and (3). Such differences are not observed. The results can be rationalized by supposing that transition-state energies for ethanolysis are more important factors than those of the ground state.

**Comment**

It has been argued that bond lengths can be directly correlated with reactivity (Edwards *et al.*, 1986). Aryloxy derivatives of 5-phenyltetrazole and benzisothiazole 1,1-dioxide have been shown to possess unusual C—O—C ether bonds, in which one C—O bond to the aryl group is exceptionally long and the other C—O bond to the heteroaromatic system is exceptionally short (Brigas & Johnstone, 1996; Alves *et al.*, 1996, 1997). Typically, the long single bond has a bond order  $n < 1$  and the short single bond has a bond order  $n = 1.3–1.4$ . Partly for these reasons, oxidative addition during catalytic hydrogenolysis occurs across the weaker longer bond, such that the aryloxy derivatives give high yields of arenes (Brigas & Johnstone, 1990; Alves *et al.*, 1997). However, for nucleophilic attack on the same aryloxy ethers, it could be expected that the C atom of the C—O—C bond which lies in the heteroaromatic system [*e.g.* C3 in (1)] would be positively charged

and much more susceptible to nucleophilic attack than the other C atom of the ether linkage [*e.g.* C1' in (1)] (Alves *et al.*, 1997). EEM (electronegativity equalization method) and Gaussian calculations provide support for this supposition (Alves, 1996). To test this hypothesis experimentally, two aryloxy derivatives, (1) and (3), of benzisothiazole 1,1-dioxide were refluxed with ethanol.



Compound (1) contains an electron-withdrawing nitro group in the *para* position, while compound (3) contains an electron-donating methoxy group in the *para* position. With ethanol, compound (1) was converted very rapidly into the ethoxy compound (2), but compound (3) was unchanged at the same temperature when refluxed for a considerably longer time. Thus, nucleophilic displacement of 4-nitrophenol [(4),  $R = \text{NO}_2$ ] from ether (1) by ethanol was easy and gave the ethyl ether (2). Similar displacement of 4-methoxyphenol [(4),  $R = \text{OCH}_3$ ] from ether (3) did not occur. The effects are comparable with those observed for aryl trifluoromethanesulfonates (Zhu *et al.*, 1997). The results might be rationalized by invoking a double action from two strongly electron-withdrawing effects at C3 of ether (1), one due to the 4-nitrophenoxy group and the other due to the 'electron-deficient' heteroaromatic system. In the case of ether (3), the 4-methoxyphenoxy group would be expected to offset the electron-withdrawing heteroaromatic system, thereby reducing the charge density at C3 of the heteroaromatic system and making nucleophilic attack more difficult. With this explanation, nucleophilic attack by ethanol would be expected to be easier for the more electropositive C3 atom in ether (1) but would be more difficult for C3 in ether (3). It would be expected that these same effects should cause a difference in the relative C—O—C bond lengths in compounds (1) and (3), since bond length is related to reactivity and electronegativity (Peter, 1986). However, comparison of the ether bond lengths reveals no significant differences in ethers (1) or (3). Thus, for these two ethers, the pairs of ether C—O bond lengths are 1.335 (3) and 1.417 (3) Å (this work), and 1.331 (3) and 1.424 (3) Å, respectively (Brigas & Johnstone, 1996), suggesting that the opposite electronic effects of the nitro and methoxy groups actually have no opposed effects on the C—O—C ether bond lengths or angles. If an explanation for

easy solvolysis cannot be found in ground-state electronic features in ethers (1) and (3), then the transition-state structures (5) must be important. In a fully developed *S<sub>N</sub>Ar* transition state [(5), *R* = NO<sub>2</sub>], a resonance-stabilized 4-nitrophenol provides a far better leaving group than does a resonance-destabilized 4-methoxyphenol [(5), *R* = OCH<sub>3</sub>], suggesting that the transition-state energy for solvolysis is significantly greater for the ether (3) than for (1) and that the different rates of solvolysis are due mostly to this factor.

The ethoxy ether product of solvolysis (2) has C—O—C ether bond lengths in keeping with those expected for such a compound having an *sp*<sup>3</sup>-C atom in place of C1' (Barkley *et al.*, 1997). Therefore, the product of solvolysis is not expected to enhance or diminish any differences found in the transition- or ground-state energies for ethers (1) or (3).

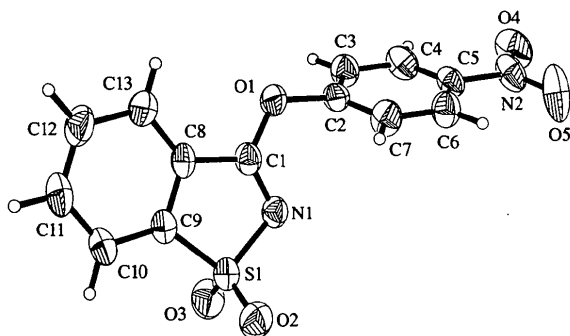


Fig. 1. Perspective view of (1) showing 50% probability displacement ellipsoids.

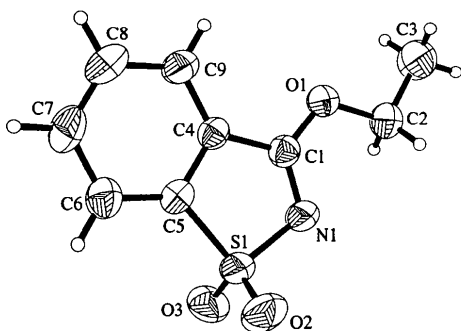


Fig. 2. Perspective view of compound (2) showing 50% probability displacement ellipsoids.

## Experimental

3-(4-Nitrophenoxy)-1,2-benzisothiazole 1,1-dioxide, (1), was prepared from pseudosaccharyl chloride and 4-nitrophenol according to a method described previously (Brigas & Johnstone, 1990). M.p. 519–520 K. Elemental analysis: found C 52.0, H 2.9, N 8.7%; C<sub>13</sub>H<sub>8</sub>NO<sub>5</sub>S requires C 51.3, H 2.7, N 9.2%. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO]: δ 8.20 (2H, *d*, *J* = 9.7 Hz, ArH), 7.82–

6.62 (4H, *m*, ArH), 7.42 p.p.m. (2H, *d*, *J* = 9.7 Hz, ArH). MS: *m/z* 304 (*M*<sup>+</sup>). IR  $\nu_{\max}$ : 1554, 1531, 1378, 1353, 1175 and 855 cm<sup>-1</sup>. Analytical data for 3-ethoxy-1,2-benzisothiazole 1,1-dioxide, (2), and 3-(methoxyphenoxy)-1,2-benzisothiazole 1,1-dioxide, (3), have been published recently (Alves *et al.*, 1997; Brigas & Johnstone, 1996). For solvolysis studies, the ether, (1) or (3), was refluxed in a large relative molar excess of ethanol. Within 30 min, the ether (1) had been converted into the ethoxy compound (2) in a yield close to 100%. In contrast, after 5 h of reflux in ethanol, the ether (3) gave no evidence for formation of the ether (2) and was recovered unchanged.

## Compound (1)

### Crystal data

C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>5</sub>S  
*M<sub>r</sub>* = 304.27  
 Orthorhombic  
*Pbca*  
*a* = 13.803 (3) Å  
*b* = 10.780 (16) Å  
*c* = 17.272 (7) Å  
*V* = 2570 (4) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.573 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 10.2–19.1°

$\mu$  = 0.276 mm<sup>-1</sup>

*T* = 293 (2) K

Prism

0.30 × 0.30 × 0.30 mm

Colourless

### Data collection

Rigaku AFC-6S diffractometer

$\omega$ -2 $\theta$  scans

Absorption correction: none

2256 measured reflections

2256 independent reflections

1552 reflections with

*I* > 2 $\sigma$ (*I*)

$\theta_{\max}$  = 24.95°

*h* = -16 → 0

*k* = 0 → 12

*l* = 0 → 20

3 standard reflections

every 150 reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.039

*wR*(*F*<sup>2</sup>) = 0.107

*S* = 1.023

2256 reflections

191 parameters

H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[ $\sigma^2$ (*F<sub>o</sub>*<sup>2</sup>) + (0.033*P*)<sup>2</sup> + 1.37*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta/\sigma$ )<sub>max</sub> = 0.001

$\Delta\rho_{\max}$  = 0.24 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.30 e Å<sup>-3</sup>

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.0024 (4)

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—N1	1.664 (2)	C1—C8	1.477 (3)
S1—C9	1.766 (3)	C2—C3	1.364 (4)
O1—C1	1.335 (3)	C2—C7	1.371 (4)
O1—C2	1.417 (3)	C8—C9	1.381 (4)
N1—C1	1.279 (3)		
N1—S1—C9	96.24 (13)	C3—C2—C7	122.7 (3)
C1—O1—C2	118.7 (2)	C3—C2—O1	117.5 (3)
C1—N1—S1	108.40 (18)	C7—C2—O1	119.7 (2)
N1—C1—O1	124.4 (2)	C9—C8—C1	108.8 (2)
N1—C1—C8	119.3 (2)	C8—C9—S1	107.24 (19)
O1—C1—C8	116.3 (2)		

**Compound (2)***Crystal data*

C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>S  
*M<sub>r</sub>* = 211.23  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 7.149 (4) Å  
*b* = 8.178 (5) Å  
*c* = 16.556 (3) Å  
 $\beta$  = 93.15 (3)°  
*V* = 966.5 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.452 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

*Data collection*

Rigaku AFC-6S diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 1699 measured reflections  
 1699 independent reflections  
 1133 reflections with  
 $I > 2\sigma(I)$

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.044  
*wR*(*F*<sup>2</sup>) = 0.108  
*S* = 1.025  
 1699 reflections  
 127 parameters  
 H atoms treated by a  
 mixture of independent  
 and constrained refinement

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25  
 reflections  
 $\theta$  = 3.5–7.4°  
 $\mu$  = 0.314 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.35 × 0.25 × 0.20 mm  
 Colourless

$\theta_{\max}$  = 24.98°  
 $h$  = 0 → 8  
 $k$  = 0 → 9  
 $l$  = -19 → 19  
 3 standard reflections  
 every 150 reflections  
 intensity decay: <1%

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.48P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

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

S1—N1	1.645 (3)	N1—C1	1.291 (4)
S1—C5	1.760 (3)	C1—C4	1.469 (4)
O1—C1	1.311 (3)	C2—C3	1.481 (5)
O1—C2	1.466 (4)	C4—C5	1.384 (4)
N1—S1—C5	96.46 (13)	O1—C2—C3	107.4 (3)
C1—O1—C2	116.3 (2)	C5—C4—C1	109.0 (3)
C1—N1—S1	109.0 (2)	C4—C5—S1	107.1 (2)
N1—C1—O1	123.8 (3)	C8—C7—C6	121.1 (3)
N1—C1—C4	118.4 (3)	C9—C8—C7	121.5 (3)
O1—C1—C4	117.8 (3)	C4—C9—C8	117.8 (3)

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1995a); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995b); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL97*.

The authors thank the Eschenmoser Trust (UK) and JNICT (Portugal) for financial assistance.

Supplementary data for this paper are available from the IUCR electronic archives (Reference: BM1162). Services for accessing these data are described at the back of the journal.

**References**

- Alves, J. A. C. (1996). PhD thesis, Faculty of Science, University of Liverpool, England.  
 Alves, J. A. C., Barkley, J. V., Brigas, A. F. & Johnstone, R. A. W. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 669–677.  
 Alves, J. A. C., Brigas, A. F. & Johnstone, R. A. W. (1996). *Acta Cryst. C52*, 1576–1579.  
 Barkley, J. V., Cristiano, M. L. S., Johnstone, R. A. W. & Loureiro, R. M. S. (1997). *Acta Cryst. C53*, 383–386.  
 Brigas, A. F. & Johnstone, R. A. W. (1990). *Tetrahedron Lett.* **31**, 5789–5790.  
 Brigas, A. F. & Johnstone, R. A. W. (1996). *Acta Cryst. C52*, 1293–1296.  
 Edwards, M. R., Jones, P. G. & Kirby, A. J. (1986). *J. Am. Chem. Soc.* **108**, 7076–7073.  
 Molecular Structure Corporation (1995a). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Molecular Structure Corporation. (1995b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Peter, L. (1986). *J. Chem. Educ.* **63**, 123–124.  
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Zhu, J., Bigot, A. & Dau, M. E. T. H. (1997). *Tetrahedron Lett.* **38**, 1181–1182.

*Acta Cryst.* (1998). **C54**, 253–256

**Complex Network of Hydrogen Bonds in 3-Aminopyrazole-4-carboxylic Acid**

ALLISON J. DOBSON AND ROGER E. GERKIN

*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu*

(Received 9 June 1997; accepted 6 October 1997)

**Abstract**

3-Aminopyrazole-4-carboxylic acid, C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>, crystallized in the non-centrosymmetric space group *P*2<sub>1</sub> in the zwitterionic form. Intermolecular N—H···O hydrogen bonds with N···O distances of 2.768 (2) and 2.747 (2) Å link molecules into two sets of chains propagating along [1 $\bar{1}$ 0] and [110]. The two sets of chains are crosslinked by strong hydrogen bonds. A complex network of hydrogen bonds ensues. There is a single intramolecular