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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)

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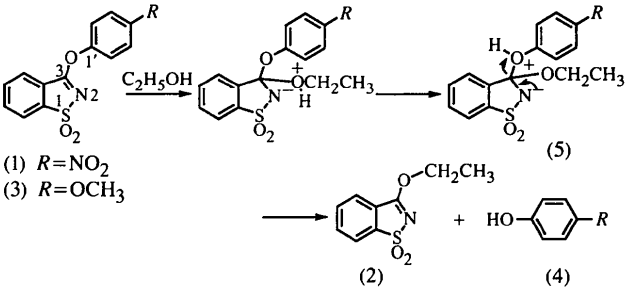
Abstract

The bond lengths in the central C—O—C ether linkage of title compound (1), $C_{13}H_8N_2O_5S$, 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), $C_9H_9NO_3S$, 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), $R = NO_2$] from ether (1) by ethanol was easy and gave the ethyl ether (2). Similar displacement of 4-methoxyphenol [(4), $R = OCH_3$] 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

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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_NAr transition state [(5), R = NO_2], a resonance-stabilized 4-nitrophenol provides a far better leaving group than does a resonance-destabilized 4-methoxyphenol [(5), R = OCH_3], 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^3-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).

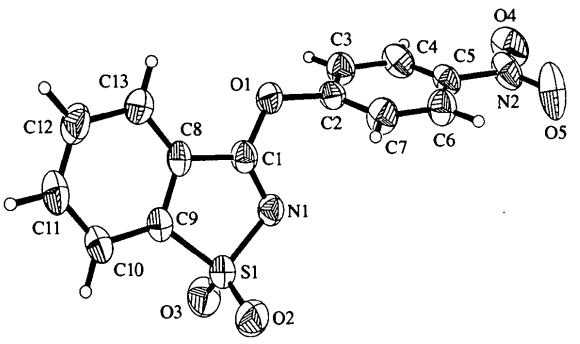

Fig. 1. Perspective view of (1) showing 50% probability displacement ellipsoids.

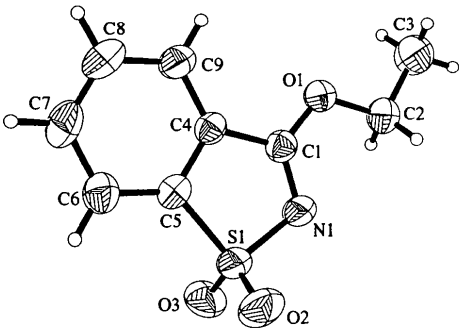

Fig. 2. Perspective view of compound (2) showing 50% probability displacement ellipsoids.

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%; $C_{13}H_8NO_5S$ requires C 51.3, H 2.7, N 9.2%. ^{1}H NMR [$(CD_3)_2SO$]: 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^+). IR ν_{max}: 1554, 1531, 1378, 1353, 1175 and 855 cm^{-1}. 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

$C_{13}H_8N_2O_5S$	Mo $K\alpha$ radiation
M_r = 304.27	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
Pbca	θ = 10.2–19.1°
a = 13.803 (3) Å	μ = 0.276 mm^{-1}
b = 10.780 (16) Å	T = 293 (2) K
c = 17.272 (7) Å	Prism
V = 2570 (4) Å^3	0.30 × 0.30 × 0.30 mm
Z = 8	Colourless
D_x = 1.573 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-6*S* diffractometer	θ_{max} = 24.95°
ω–2θ scans	h = −16 → 0
Absorption correction: none	k = 0 → 12
2256 measured reflections	l = 0 → 20
2256 independent reflections	3 standard reflections every 150 reflections
1552 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$wR(F^2)$ = 0.107	$\Delta\rho_{min}$ = −0.30 e Å^{-3}
S = 1.023	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
2256 reflections	Extinction coefficient: 0.0024 (4)
191 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms treated by a mixture of independent and constrained refinement	
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 1.37P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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

$C_9H_9NO_3S$
M_r = 211.23
Monoclinic
$P2_1/n$
a = 7.149 (4) Å
b = 8.178 (5) Å
c = 16.556 (3) Å
β = 93.15 (3)°
V = 966.5 (8) Å^3
Z = 4
D_x = 1.452 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3.5–7.4°
μ = 0.314 mm^{-1}
T = 293 (2) K
Prism
0.35 × 0.25 × 0.20 mm
Colourless

Data collection

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

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

Refinement

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

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.48P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e 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: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995*b*); 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*.

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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.

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

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Abstract

3-Aminopyrazole-4-carboxylic acid, $C_4H_5N_3O_2$, crystallized in the non-centrosymmetric space group $P2_1$ 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