the Patterson method and refined by full-matrix least-squares techniques. For all non-H atoms, anisotropic displacement parameters were refined, except the disordered parts of I2 and I3. Two pairs of peaks in the difference electron-density map relating to I2 and I3 were refined as disordered parts of these ions, with site occupations of 80% for both I2 and I3. For the isotropically refined split positions I2*A*, I2*B*, I3*A* and I3*B*, 10% site occupations were assumed according to their isotropic displacement parameter values from a previous refinement. Test refinements in which these peaks were treated as parts of water O atoms, assuming a statistical disorder between I^- ions and water, failed completely. The cyclohexane H atoms H1 to H6 and the hydroxy H atoms H2O, H4O and H6O were refined with individual isotropic displacement parameters. The H-atom positions of the methyl groups were geometrically idealized and their isotropic displacement parameters were assigned as $1.5U_{eq}$ of the preceding C atom. Only one water H atom could be located in the difference electron-density map, but it was not refined.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976); *SCHAKAL*86 (Keller, 1986). Software used to prepare material for publication: CIF (Hall, Allen & Brown, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(4-Methoxyphenoxy)-1,2-benzisothiazole 1,1-Dioxide: its Relation to Mechanistic Behaviour in Catalytic Transfer Hydrogenolysis

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Abstract

Conjugation of oxygen with an aromatic ring, as in a phenol, gives a C—O bond length of about 1.35 Å, whereas the C—O bond length in an aliphatic alcohol is about 1.45 Å. A saccharyl ether derivative of a phenol changes the phenolic C—O bond length to 1.42 Å and makes the bond chemically more susceptible

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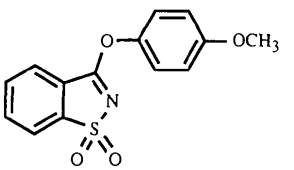
to catalytic *ipso* replacement of the aromatic C—OH linkage by C—H. The present study of the title compound, $C_{14}H_{11}NO_4S$, was carried out in order to examine specifically the effect of saccharyl ether formation on the C—O bond length of a phenol.

Comment

Derivatives of saccharin are known for their biological activity (Strupczewski *et al.*, 1995). The saccharyl heterocyclic system (1,2-benzisothiazole 1,1-dioxide) has also been used as a leaving group in important chemical transformations such as the derivatization of phenols prior to their conversion to arenes by heterogeneous catalytic transfer hydrogenolysis (Brigas & Johnstone, 1990) and for C—C bond formation from alkyl to arene by cross-coupling with zinc and tin organometallic reagents (Brigas & Johnstone, 1994). Phenolic saccharyl ethers such as the title compound, 3-(4-methoxyphenoxy)-1,2-benzisothiazole 1,1-dioxide, (1), are easily obtained by reaction of 3-chloro-1,2-benzisothiazole 1,1-dioxide with a phenol in the presence of a base.



(1)

Considering the difficulties in the investigation of reaction mechanisms in heterogeneously catalyzed liquid-phase reactions (Brigas & Johnstone, 1992), any structural information on an effect of the saccharyl part of the ether on the original phenol is potentially important. The present study was carried out in order to examine specifically the effect of saccharyl ether formation on the C—O bond length of a phenol. From chemical investigations, it is already clear that a good leaving group for catalytic hydrogenolysis, whether saccharyl or some other, such as tetrazolyl, should have an N atom near the C—O bond which is to be cleaved, possibly to aid coordination of the saccharyl ether to the dispersed metal of the catalyst, as the ether adsorbs onto its surface.

The strong electron-withdrawing effect of the saccharyl group is well known and is thought to be caused by the SO_2 group conjugated with the N atom in the isothiazole part of the molecule (Pain, Peart & Wooldridge, 1984). Therefore, in an ether formed from a phenol and a saccharyl group, as in (1), there will be competition from the aromatic ring of the original phenol, 4-methoxyphenyl in this case, and the saccharyl group for the lone-pair electrons sited on the central O atom. This effect should be reflected in the lengths of the two C—O bonds of the ether link. If the ether O atom is conjugated with one or both of the aromatic systems to which it is joined, then the C—O bond length can be expected to shorten from something close to a single bond to something more like the length of a fully conjugated phenolic C—O bond. It would not be expected to shorten to a length similar to that found in carbonyl groups (1.22 Å). In fact, the present crystal structure determination of (1) (Fig. 1) shows that there is a long C—O bond [C8—O1 1.424 (3) Å] involving the original phenol and a short C—O bond [C7—O1 1.331 (3) Å] for the saccharyl link. It is evident that, when compared with the mean length of 1.36 Å for a typical phenolic C—O bond (Allen *et al.*, 1987), the phenolic C—O link has lengthened to a value close to that found in an aliphatic alcohol, typically 1.42 Å (Allen *et al.*, 1987). The C—O link to the saccharyl system, however, is close to those found in conjugated phenolic C—O systems. Therefore, the electronic effect of the saccharyl group on the original phenol C—O bond has been to draw off its conjugative part and to convert it essentially into a single C—O bond typical of unconjugated systems. In fact, the effect is quite dramatic, with the bond changing from one representing considerable conjugation of the phenolic O atom into the aromatic ring to one in which there appears to be no conjugation whatsoever. The aromatic (phenolic) and saccharyl rings remain typical of fully conjugated flat π systems, having bond lengths and angles close to those expected.

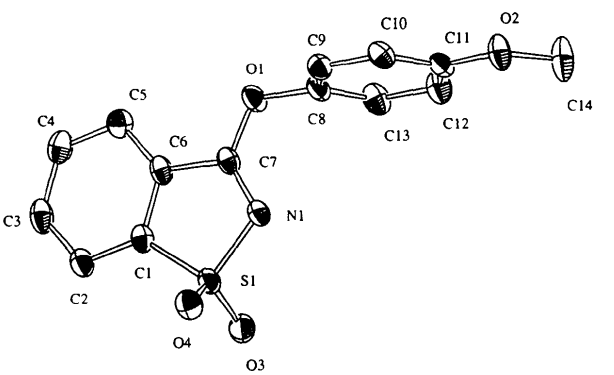


Fig. 1. Perspective view of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The torsion angles C7—O1—C8—C9 and C7—O1—C8—C13 indicate that the planes of the benzisothiazole and phenyl groups of (1) are not coplanar but are at a mutual angle of almost 90°. This means there can be no extended conjugation from one aromatic system to the other; the conjugation from the O atom must go to only one of the aromatic systems and the results show this to be the saccharyl ring. An interesting feature of the 1,2-benzisothiazole system is the narrow C1—S1—N1 angle of 96.2 (2)° in the isothiazole ring, similar to

the value of 92.7 (1)° found in saccharin itself (Bart, 1968), as a result of a compromise between ring strain and angular conformation.

Experimental

A mixture of 3-chloro-1,2-benzisothiazole 1,1-dioxide (5.2 g, 26 mmol), 4-methoxyphenol (3.2 g, 26 mmol) and triethylamine (6 ml) in toluene (100 ml) was stirred under reflux for 2 h. The mixture was filtered, diluted with dichloromethane (200 ml), washed with dilute HCl and aqueous sodium hydrogen carbonate solution, and dried (Na_2SO_4). After filtration and evaporation of the solvent from the filtrate, the residual yellow solid obtained was recrystallized from toluene to afford the desired product as white needles (87% yield; m.p. 458–459 K). Analysis: found C 58.2, H 3.8, N 4.7%; $C_{14}H_{11}NO_4S$ requires C 58.1, H 3.8, N 4.8%. ^{1}H NMR [$(CD_3)_2SO$]: δ 7.95–7.79 (4H, *m*, ArH), 7.39 (2H, *d*, J = 9.5 Hz, ArH), 7.12 (2H, *d*, J = 9.5 Hz, ArH), 3.83 p.p.m. (3H, *s*, CH_3). ν_{max}: 1620, 1554, 1505, 1381, 1334, 1170 and 838 cm^{-1}. MS: m/z 289 (M^+).

Crystal data

$C_{14}H_{11}NO_4S$
M_r = 289.31
Triclinic
$P\bar{1}$
a = 8.925 (5) Å
b = 10.301 (3) Å
c = 8.179 (4) Å
α = 94.06 (3)°
β = 115.89 (4)°
γ = 98.45 (3)°
V = 661.4 (6) Å^3
Z = 2
D_x = 1.452 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10–17°
μ = 0.2446 mm^{-1}
T = 153 K
Plate
0.35 × 0.25 × 0.10 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2481 measured reflections
2320 independent reflections
1772 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.022
θ_{max} = 24.94°
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: 0.2%

Refinement

Refinement on F
R = 0.0358
wR = 0.0423
S = 1.609
1772 reflections
181 parameters
H atoms were obtained from a difference map and their parameters were not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.46
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	0.74178 (8)	0.40953 (6)	0.12519 (8)	0.0266 (3)
O1	0.3325 (2)	0.1708 (2)	−0.0485 (2)	0.0317 (2)
O2	0.1041 (2)	−0.0048 (2)	−0.7854 (2)	0.0377 (1)
O3	0.8915 (2)	0.3557 (2)	0.1664 (2)	0.0363 (1)
O4	0.7410 (2)	0.5383 (2)	0.0697 (2)	0.0383 (1)
N1	0.5738 (3)	0.3027 (2)	−0.0332 (3)	0.0267 (1)
C1	0.6822 (3)	0.3971 (2)	0.3052 (3)	0.0270 (1)
C2	0.7644 (3)	0.4556 (3)	0.4873 (3)	0.0313 (1)
C3	0.6878 (4)	0.4198 (3)	0.5971 (3)	0.0361 (2)
C4	0.5333 (4)	0.3308 (3)	0.5261 (4)	0.0394 (2)
C5	0.4502 (3)	0.2751 (3)	0.3423 (3)	0.0345 (2)
C6	0.5283 (3)	0.3088 (2)	0.2332 (3)	0.0268 (1)
C7	0.4769 (3)	0.2601 (2)	0.0389 (3)	0.0254 (1)
C8	0.2793 (3)	0.1252 (3)	−0.2375 (3)	0.0289 (1)
C9	0.1691 (3)	0.1874 (3)	−0.3669 (3)	0.0320 (1)
C10	0.1124 (3)	0.1410 (3)	−0.5503 (3)	0.0300 (1)
C11	0.1665 (3)	0.0321 (3)	−0.6020 (3)	0.0286 (1)
C12	0.2785 (3)	−0.0296 (3)	−0.4684 (4)	0.0360 (2)
C13	0.3350 (3)	0.0183 (3)	−0.2844 (3)	0.0347 (2)
C14	0.1497 (4)	−0.1195 (3)	−0.8468 (4)	0.0539 (2)

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

S1—O3	1.435 (2)	O2—C11	1.354 (3)
S1—O4	1.432 (2)	O2—C14	1.432 (3)
S1—N1	1.659 (2)	N1—C7	1.288 (3)
S1—C1	1.777 (3)	C1—C6	1.383 (4)
O1—C7	1.331 (3)	C6—C7	1.473 (3)
O1—C8	1.424 (3)		
O3—S1—O4	117.3 (1)	S1—C1—C6	107.0 (2)
O3—S1—N1	109.3 (1)	C1—C6—C7	109.1 (2)
O3—S1—C1	110.2 (1)	O1—C7—N1	124.6 (2)
O4—S1—N1	109.3 (1)	O1—C7—C6	116.2 (2)
O4—S1—C1	112.5 (1)	N1—C7—C6	119.1 (2)
N1—S1—C1	96.2 (2)	O1—C8—C9	118.6 (2)
C7—O1—C8	116.8 (2)	O1—C8—C13	119.3 (2)
C11—O2—C14	117.9 (2)	O2—C11—C10	115.4 (2)
S1—N1—C7	108.6 (2)		
S1—N1—C7—O1	−178.5 (2)	N1—C7—O1—C8	−3.2 (3)
S1—N1—C7—C6	−0.4 (3)	C1—S1—N1—C7	0.5 (2)
O1—C7—C6—C1	178.2 (2)	C7—O1—C8—C9	−93.7 (3)
O3—S1—N1—C7	114.5 (2)	C7—O1—C8—C13	88.5 (3)
O4—S1—N1—C7	−115.9 (2)		

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

The authors thank the Eschenmoser Trust (UK) and JNICT (Portugal) for financial support (AFB) and Mr James V. Barkley for expert technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(9*S*,9a*R*)-1,3,4,6,7,8,9,9a-Octahydro-2*H*-quinolizine-1-spiro-2′-(1′,3′-dithiane)-9-carbonitrile

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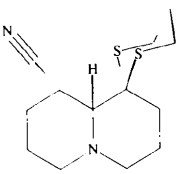
Abstract

The title compound, $C_{13}H_{20}N_2S_2$, was prepared during the intramolecular addition of dithiane anions to unsaturated nitriles. The octahydroquinolizine ring adopts a chair–chair conformation with the dithiane ring in a chair conformation oriented distal to the nitrile moiety.

Comment

The intramolecular cyclization of dithiane anions has been used to assemble rapidly cyclopentyl ketones (Grotjahn & Andersen, 1981) and alcohols (Davey & Taylor, 1987), but is complicated by the competitive reaction of the base with the cyclization precursor. To demonstrate the superiority of the nitrile group for these cyclizations, we prepared the title compound, (I), from 1-[3-(1,3-dithian-2-yl)propyl]-3-cyano-1,4,5,6-tetrahydropyridine by treatment with *n*-butyllithium. A mixture of octahydroquinolizine epimers was obtained, from which the title compound was separated by selective extraction and crystallization.



(I)

The X-ray structure is similar to that of the 1-azabicyclo[4.4.0]decane borine adduct that has been described recently (Tham & White, 1994). In the two cases the octahydroquinolizine rings adopt chair conformations typical of these alkaloids. The metrical parameters of the rings are quite similar, except at the points of substitution (C2, C9 and N2 in the present structure); at these positions the distances are longer in the substituted case. Thus, the average distances for C2—C3 and C8—C9 [1.535 (4) Å] and for C2—C10 and C9—C10 [1.550 (4) Å] in the present structure

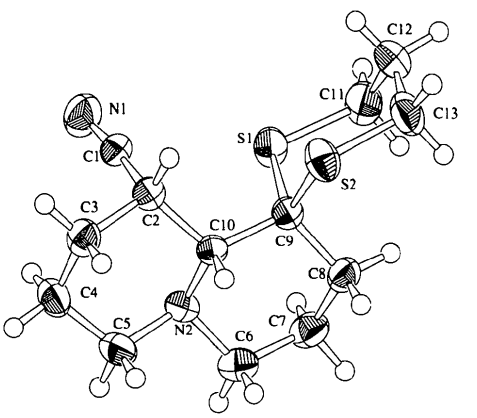


Fig. 1. Perspective drawing of the title compound with displacement ellipsoids drawn at the 50% probability level.

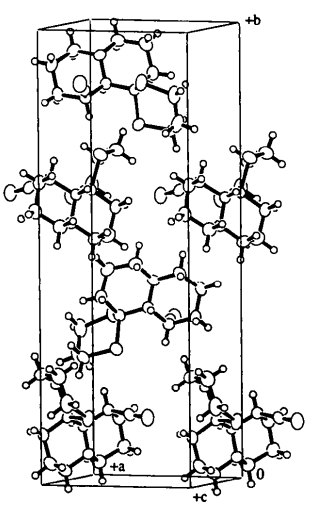


Fig. 2. Packing diagram of the title compound with displacement ellipsoids drawn at the 50% probability level.