Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.150$
$S = 1.079$
8434 reflections
528 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.5786P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1996)
Extinction coefficient: 0.0196 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1*A*—C1*A*	1.340 (2)	O1*B*—C1*B*	1.346 (2)
O2*A*—C4*A*	1.335 (2)	O2*B*—C4*B*	1.343 (2)
O3*A*—C13*A*	1.244 (2)	O3*B*—C13*B*	1.242 (2)
O4*A*—C6*A*	1.240 (2)	O4*B*—C6*B*	1.247 (2)
C9*A*—C10*A*	1.316 (3)	C9*B*—C10*B*	1.316 (3)
C8*A*—C15*A*—C11*A*	94.33 (15)	C8*B*—C15*B*—C11*B*	93.2 (2)
C12*A*—C7*A*—C8*A*—C9*A*	66.7 (2)		
C12*A*—C7*A*—C8*A*—C15*A*	−37.2 (2)		
C15*A*—C8*A*—C9*A*—C10*A*	32.1 (2)		
C7*A*—C8*A*—C9*A*—C10*A*	−71.1 (2)		
C8*A*—C9*A*—C10*A*—C11*A*	0.6 (2)		
C9*A*—C10*A*—C11*A*—C15*A*	−32.9 (2)		
C9*A*—C10*A*—C11*A*—C12*A*	70.4 (2)		
C8*A*—C7*A*—C12*A*—C11*A*	0.7 (2)		
C10*A*—C11*A*—C12*A*—C7*A*	−67.8 (2)		
C15*A*—C11*A*—C12*A*—C7*A*	36.0 (2)		
C9*A*—C8*A*—C15*A*—C11*A*	−48.6 (2)		
C7*A*—C8*A*—C15*A*—C11*A*	59.0 (2)		
C10*A*—C11*A*—C15*A*—C8*A*	49.0 (2)		
C12*A*—C11*A*—C15*A*—C8*A*	−58.6 (2)		
C12*B*—C7*B*—C8*B*—C9*B*	69.8 (2)		
C12*B*—C7*B*—C8*B*—C15*B*	−34.7 (2)		
C15*B*—C8*B*—C9*B*—C10*B*	34.1 (3)		
C7*B*—C8*B*—C9*B*—C10*B*	−70.2 (2)		
C8*B*—C9*B*—C10*B*—C11*B*	−0.7 (3)		
C9*B*—C10*B*—C11*B*—C15*B*	−32.6 (3)		
C9*B*—C10*B*—C11*B*—C12*B*	71.1 (2)		
C8*B*—C7*B*—C12*B*—C11*B*	−3.2 (2)		
C10*B*—C11*B*—C12*B*—C7*B*	−64.6 (2)		
C15*B*—C11*B*—C12*B*—C7*B*	39.8 (2)		
C9*B*—C8*B*—C15*B*—C11*B*	−49.9 (2)		
C7*B*—C8*B*—C15*B*—C11*B*	58.3 (2)		
C10*B*—C11*B*—C15*B*—C8*B*	49.4 (2)		
C12*B*—C11*B*—C15*B*—C8*B*	−60.5 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1O*A*···O3*A*	0.99 (3)	1.63 (3)	2.526 (2)	148 (2)
O1*B*—H1O*B*···O3*B*	1.10 (4)	1.52 (4)	2.530 (2)	149 (4)
O2*A*—H2O*A*···O4*A*	0.96 (3)	1.64 (3)	2.514 (3)	148 (2)
O2*B*—H2O*B*···O4*B*	0.96 (4)	1.65 (3)	2.529 (3)	150 (3)

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm ($2\theta_{\max} = 66.37°$) and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. Only reflections with $2\theta < 62°$ were used for the refinement.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically. C—H distances range from 0.93 (2) to 1.02 (3) Å and $U_{\rm iso}$ values for H atoms range from 0.49 (6) to 0.15 (2) Å^2.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SAINT* (Siemens, 1996*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1163). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Cheng, R. K. Y. & Cheng, C. C. (1978). *J. Med. Chem.* **21**, 291–294.
Majumdar, G., Murty, K. V. S. N. & Mal, D. (1994). *Tetrahedron Lett.* **35**, 6139–6140.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1996). *SHELXTL Reference Manual.* Version 5.0. University of Göttingen, Germany.
Siemens (1996*a*). *SMART Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SAINT Software Reference Manual.* Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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5-Benzyloxy-1-phenyltetrazole: catalytic transfer hydrogenolysis of benzyl ethers

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Abstract

In contrast to the earlier reported inertness of 5-benzyloxy-1-phenyltetrazole, (1*a*), and 3-benzyloxy-1,2-benzisothiazole 1,1-dioxide, (2*a*), towards catalytic

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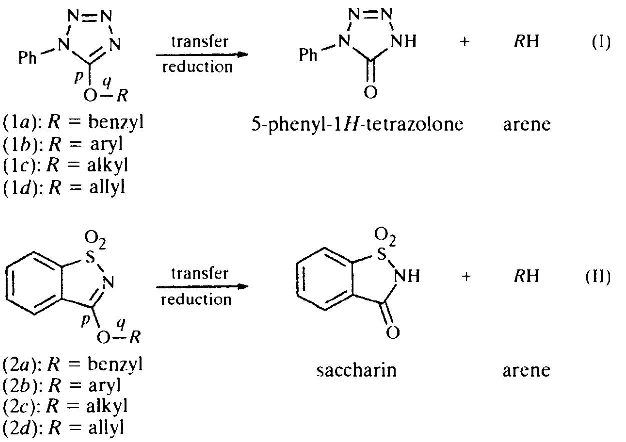
transfer hydrogenolysis in toluene/water solvent systems, it is now shown that simply changing the solvent to tetrahydrofuran/water leads to their rapid hydrogenolysis with formation of toluene. Compound (1*a*), $C_{14}H_{12}N_4O$, has a short C—O ether bond to the tetrazole ring [1.3261 (15) Å] and a particularly long C—O bond to the benzyl group [1.4676 (16) Å], consistent with an activation of this longer bond by the strongly electronegative tetrazole unit.

Comment

It has been proposed, and demonstrated, that bond lengths are related to chemical reactivity (Bürgi & Dunitz, 1987; Edwards *et al.*, 1986). Structures of aryl, alkyl and allyl ethers, (1*b*)–(1*d*) and (2*b*)–(2*d*), have been determined by X-ray crystallography (Alves *et al.*, 1997; Brigas & Johnstone, 1996; Barkley *et al.*, 1997; Brigas *et al.*, 1998, 1997). Generally, it is found that the ether linkage in aryl compounds (1*b*) and (2*b*) has a very short C—O bond (*p*, approximately 1.32 Å) to the heteroaromatic group and a very long C—O ether bond (*q*, approximately 1.46 Å) to the aryl group. The combined length of the C—O—C bonds (*p* + *q*) in ethers (1*b*)–(1*d*) and (2*b*)–(2*d*) is remarkably constant at about 2.78 Å, the two bonds being strongly negatively correlated. On the basis of these results, it was suggested that bond lengths did reflect chemical reactivity in the series of ethers (1) and (2) (Alves *et al.*, 1997).



Considered as 'alkyl' ethers, and by comparison with (1*c*) and (2*c*), the benzylic compounds (1*a*) and (2*a*) might be expected to be inert to hydrogenolysis (Johnstone *et al.*, 1985; Alves *et al.*, 1997). Alternatively, benzylic compounds are known to add oxidatively to transition metals (Chaloner, 1986). Whereas benzyloxy carbonyl esters are easily hydrogenolysed catalytically by use of hydrogen itself or by transfer methods, benzyl ethers are much more resistant to transfer reduction, typically requiring several hours at elevated temperatures or the additional use of Lewis acids (Johnstone *et al.*, 1985). Therefore the benzylic ethers (1*a*) and (2*a*) might be considered to be anomalous whether they react or not, when subjected to hydrogenolysis, especially as benzyl carbamates can be readily hydrogenolysed (Jackson & Johnstone, 1976).

Heterogeneous catalytic transfer hydrogenolyses are commonly carried out in biphasic benzene/water or toluene/water solvent systems. Under such conditions, the ethers (1*a*) and (2*a*) remained unchanged over a period of 1 h, but formed some benzyl alcohol by hydrolysis. A similar result has been recorded earlier (Price, 1985). In contrast, the same ethers in a refluxing tetrahydrofuran/water biphasic solvent system with the same Pd/C catalyst and sodium phosphinate as hydrogen donor give quantitative formation of toluene in 10 min at lower temperatures (336 K), with no hydrolysis to benzyl alcohol [reactions (I) and (II); compounds (1*a*) and (2*a*)]. This effect of simply changing from one biphasic solvent system to another is remarkable in heterogeneous catalytic transfer hydrogenolysis.

The crystal structure for benzyl ether (2*a*) has been reported recently (Brigas *et al.*, 1997); the molecule has a very short bond *p* and a very long bond *q*, like others in the series of ethers (2*b*)–(2*d*), with *p* + *q* equal to 2.769 (6) Å, very similar to the aryl ethers (2*b*). Structural results for benzyl ether (1*a*) are presented here (Fig. 1, Table 1). Particularly notable are the short O—C1 and long O—C2 bonds. Indeed, although O—C1 (bond *p*) is typical of those in the series of compounds (1) and (2), O—C2 (bond *q*) is the longest such bond so far observed. The sum of these two bond lengths is 2.794 (3) Å, in line with the other compounds, (1*b*)–(1*d*).

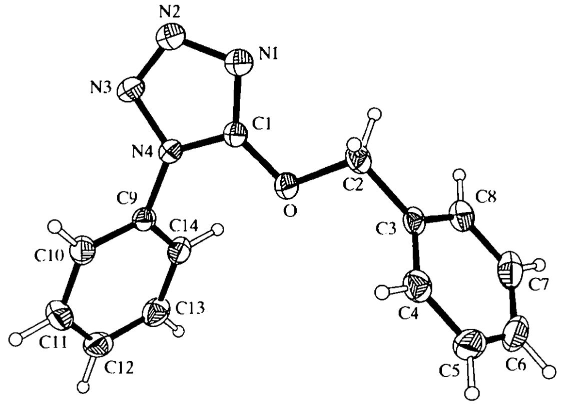


Fig. 1. The molecular structure of (1*a*) with atom labels and 50% probability ellipsoids for non-H atoms.

The geometry of the tetrazole ring is entirely typical of those previously reported, with all bond lengths and angles well within the ranges found for 245 such rings in 152 structures generated by a search of the Cambridge

Structural Database (October 1998 version; Allen & Kennard, 1993). This heterocyclic ring is essentially planar and the ether linkage lies almost in the same plane, but both phenyl groups are rotated significantly out of this plane (see torsion angles in Table 1).

Experimental

Synthesis of 5-benzyloxy-1-phenyltetrazole (1*a*): potassium *t*-butoxide (1.1 g, 9.8 mmol) was added to a stirred solution of benzyl alcohol (1.1 g, 10.17 mmol) in dry dimethyl sulfoxide (30 ml) under argon. When all the base had dissolved (10 min), 5-chloro-1-phenyltetrazole (2.0 g, 11.07 mmol) was added. The mixture was stirred at 348 K for 1 h and then poured into a large excess of ice/water. The resulting colourless solid was filtered off and dried in air. This solid was then dissolved in dichloromethane (50 ml), washed with saturated $NaHCO_3$ (3 × 20 ml) and HCl (1 *M*, 3 × 20 ml) and then dried (Na_2SO_4). After evaporation of the solvent, the residual solid was recrystallized from ethanol to afford compound (1*a*) as colourless needles (2.3 g, 88% yield; m.p. 421–422 K). Found: C 66.7, H 4.8, N 22.4%. $C_{14}H_{12}N_4O$ requires C 66.7, H 4.8, N 22.2%. ^1H NMR (300 MHz, $CDCl_3$): δ 5.18 (2H, *s*), 7.26–7.52 (8H, *m*), 7.92–7.96 (2H, *d*, J = 6.6 Hz); IR ν_{max}: i592, 1562 cm^{-1}; MS (*m/z*): 252 (M^+).

Transfer reduction of 5-benzyloxy-1-phenyltetrazole: 10% palladium-on-charcoal (36 mg) was added to a stirred solution of 5-benzyloxy-1-phenyltetrazole, (1*a*) (50 mg, 0.19 mmol), and an internal standard (xylene, 101 mg) in tetrahydrofuran (THF) (20 ml) and the mixture was heated to reflux (336 K). Sodium phosphinate (161 mg, 1.52 mmol) in distilled water (3 ml) was added and the progress of the reaction was monitored for formation of toluene by gas chromatography and for the disappearance of the starting material by thin-layer chromatography. Transfer hydrogenolysis of the starting material to form only toluene and 5-phenyl-1-tetrazolone was complete in 10 min.

Transfer reduction of 3-benzyloxy-1,2-benzisothiazole 1,1-dioxide: this was carried out as described above for 5-benzyloxy-1-phenyltetrazole but using 44 mg (0.16 mmol) of the starting thiazole 1,1-dioxide (2*a*). Conversion to toluene and saccharin was complete in 15 min at 336 K. For either compound, (1*a*) or (2*a*), carrying out the reaction in exactly the same way but omitting the sodium phosphinate gave no hydrogenolysis, thereby showing that THF itself is not a hydrogen donor in this reaction.

Crystal data

$C_{14}H_{12}N_4O$
M_r = 252.28
Monoclinic
$P2_1/c$
a = 9.5461 (15) Å
b = 6.2510 (10) Å
c = 20.773 (3) Å
β = 98.008 (4)°
V = 1227.5 (3) Å^3
Z = 4
D_x = 1.365 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 2880 reflections
θ = 2.15–28.12°
μ = 0.091 mm^{-1}
T = 160 (2) K
Plate
0.50 × 0.45 × 0.15 mm
Colourless

Data collection

Bruker AXS SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: none
7286 measured reflections
2911 independent reflections

1713 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 28.71°
$h = -12 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -11 \rightarrow 27$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.090$
$S = 0.910$
2911 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max}$ = 0.212 e Å^{-3}
$\Delta\rho_{min}$ = −0.212 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0089 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O—C1	1.3261 (15)	N2—N3	1.2904 (17)
O—C2	1.4676 (16)	N3—N4	1.3665 (15)
N1—C1	1.3159 (17)	N4—C1	1.3412 (18)
N1—N2	1.3791 (17)	C2—C3	1.498 (2)
C1—O—C2	114.28 (10)	O—C1—N4	120.73 (12)
N1—C1—O	128.72 (13)	O—C2—C3	106.99 (11)
N1—C1—N4	110.55 (12)		
C2—O—C1—N1	2.04 (19)	O—C2—C3—C8	102.69 (15)
C2—O—C1—N4	−177.99 (12)	C1—N4—C9—C14	−63.31 (19)
C1—O—C2—C3	−170.36 (11)	N3—N4—C9—C10	−62.34 (17)
O—C2—C3—C4	−77.53 (16)		

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. Coverage was essentially complete for $\theta < 26°$.

H atoms were placed geometrically and refined with a riding model, and with U_{iso} constrained to be 1.2 × U_{eq} of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1073). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Alves, J. A. C., Barkley, J. V., Brigas, A. F. & Johnstone, R. A. W. (1997). *J. Chem. Soc. Perkin Trans.* 2, pp. 669–677.

Barkley, J. V., Cristiano, M. L. S., Johnstone, R. A. W. & Loureiro, R. M. S. (1997). *Acta Cryst.* C**53**, 383–386.

Brigas, A. F., Goncalves, P. M. & Johnstone, R. A. W. (1997). *J. Chem. Soc. Perkin Trans.* 1, pp. 2603–2605.

Brigas, A. F., Goncalves, P. M. & Johnstone, R. A. W. (1998). *Acta Cryst.* C**54**, 251–253.

Brigas, A. F. & Johnstone, R. A. W. (1996). *Acta Cryst.* C**52**, 1293–1296.

Bürgi, H.-B. & Dunitz, J. D. (1987). *J. Am. Chem. Soc.* **109**, 2924–2926.

Chaloner, P. A. (1986). *Handbook of Coordination Catalysis in Organic Chemistry*, pp. 266–268; 851. London: Butterworths.

Edwards, M. R., Jones, P. G. & Kirby, A. J. (1986). *J. Am. Chem. Soc.* **108**, 7067–7073.

Jackson, A. E. & Johnstone, R. A. W. (1976). *Synthesis*, pp. 685–687.

Johnstone, R. A. W., Wilby, A. H. & Entwistle, I. D. (1985). *Chem. Rev.* **85**, 129–170.

Price, P. J. (1985). PhD thesis, University of Liverpool, England.

Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software*. Bruker AXS Inc., Madison, Wisconsin, USA.

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12-Formyl-9,10-dimethyl-9,10-dihydro-11-thia-9,10-ethanoanthracene

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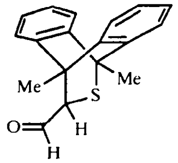
Abstract

The structure of the title compound, $C_{18}H_{16}OS$, is described. Two conformers co-exist in the crystal structure with a very near spatial arrangement.

Comment

Thiaethanoanthracenes are convenient precursors for thioaldehydes (Pelloux-Léon & Vallée, 1997). Upon heating, they undergo cyclo-reversion and give anthracene and a compound containing a carbon–sulfur double bond. The title compound, (1), is a precursor for monothioglyoxal and can also be used as an intermediate in the synthesis of various thiaethanoanthracenes (Arnaud *et al.*, 1994; Pelloux-Léon *et al.*, 1997). We have recently reported the nucleophilic attack of an enolate on the monothioglyoxal precursor (Minassian *et al.*, 1999). To understand the stereoselectivity observed in such additions, knowledge of the preferred conformation of (1) would be of interest. We have thus determined its atomic arrangement.



(1)

The present determination shows the existence of two conformers (Fig. 1) with very similar spatial conformations. Owing to this similarity, we think that both would give the same diastereoselectivity results. If one supposes that these conformers are also predominantly present in solution, then, according to Fig. 2, and assuming that the attack would occur from the less hindered side, the preferred face would be the *S* one. If the entering nucleophilic (Nu) group ranks third in the CIP priority rule (Cahn *et al.*, 1996), the relative configuration of the obtained product will be R^*,S^*. In order to simplify the text, we note the $C_{18}H_{16}OS$ conformer as *C* and the $C'_{18}H'_{16}O'S'$ conformer as *C′* hereafter.

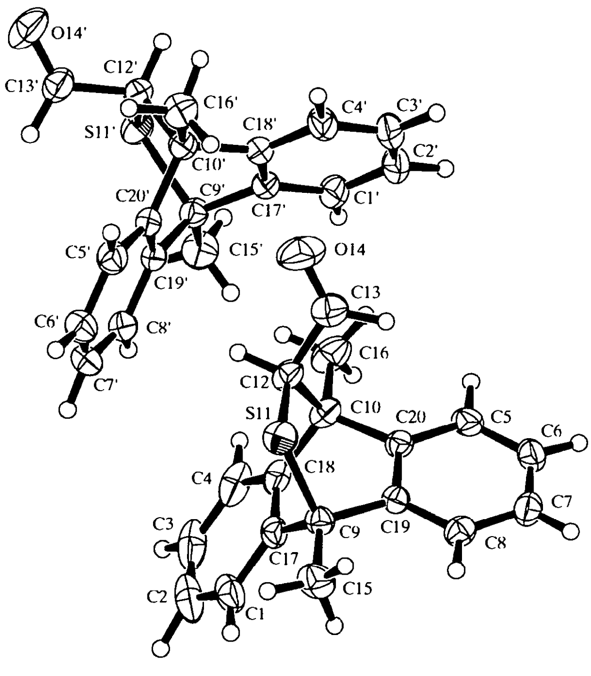


Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the two conformers of (1) shown with 40% probability displacement ellipsoids.