organic papers

6-Nitro-1-(phenylsulfonyl)-1*H*-indole

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**Key indicators**

Single-crystal X-ray study
$T = 296$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.106
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{14}H_{10}N_2O_4S$, the nitro group, confirmed as being in the 6-position, is coplanar with the indole ring system and the angle between the planes of the indole system and the phenyl ring is 96.1 (1)°.

Comment

The chemistry of 2- and 3-nitroindoles is of great interest and utility for the synthesis of carbazoles *via* Diels–Alder cyclo-addition reactions (Wenkert *et al.*, 1988; Kishbaugh & Gribble, 2001; Biolatto *et al.*, 2001), pyrrolo[3,4-*b*]indoles *via* 1,3-dipolar cycloaddition reactions with mesoionic münchnones (1,3-oxazolium-5-olates) (Gribble *et al.*, 1998, 2000), and pyrrolo[2,3-*b*]indoles and pyrrolo[3,4-*b*]indoles *via* the Barton–Zard pyrrole synthesis (Pelkey *et al.*, 1996; Pelkey & Gribble, 1997), for nucleophilic addition reactions (Pelkey *et al.*, 1999; Pelkey & Gribble, 1999) and for reduction to aminoindoles (Roy & Gribble, 2006). Although 3-nitroindoles can be synthesized by nitration of N-protected indoles (Pelkey & Gribble, 1999), an isomeric nitroindole by-product is obtained if low temperatures are not maintained (Caixach *et al.*, 1979). For example, the nitration of 1-(phenylsulfonyl)-indole with acetyl nitrate at room temperature affords 3-nitro-1-(phenylsulfonyl)indole, (I), and what we propose is 6-nitro-1-(phenylsulfonyl)indole, (II), in 71% yield in a ratio of 82 to 18. Nitration at 333 K affords these nitroindoles in a 98:2 ratio (Pelkey & Gribble, 1999). To confirm that this by-product is indeed 6-nitro-1-(phenylsulfonyl)indole, (II), we performed a crystal structure determination.
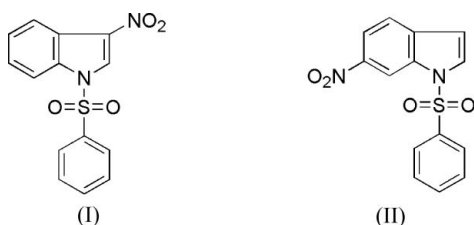
The X-ray crystallographic analysis confirms the proposed molecular structure and atom connectivity for (II) (Fig. 1). The indole ring system is planar with bond distances and angles in agreement with those of other indole derivatives (Beddoes *et al.*, 1986; Zarza *et al.*, 1988; Yokum & Fronczek, 1997; Seshadri *et al.*, 2002; Mason *et al.*, 2003; Gallagher *et al.*, 2004; Sonar *et al.*, 2004). Likewise, the geometry about the sulfonyl group is comparable to that observed in other 1-(phenylsulfonyl)indoles (Beddoes *et al.*, 1986; Yokum & Fronczek, 1997; Simon *et al.*, 2000; Seshadri *et al.*, 2002; Sonar *et al.*, 2004). The previously observed deviation of the S atom
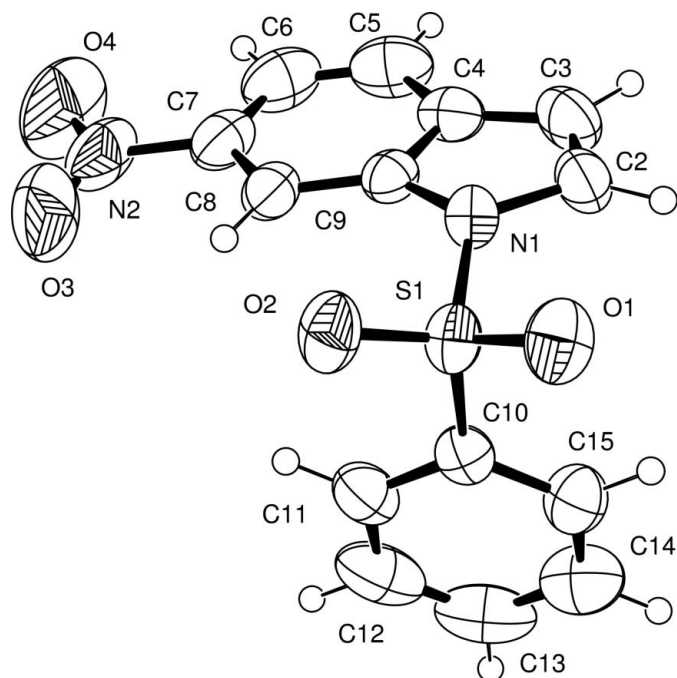
Figure 1
Molecular structure of (II), showing the atom labeling and 50% probability displacement ellipsoids.

geometry from tetrahedral is also seen in (II); O1—S1—O2 is 120.37 (14)° and O1—S1—Nl is 105.33 (13)°. The angle between the planes of the indole ring system and the phenyl ring is 96.1 (1)°. By comparison, this angle is 82.83° in 3-methyl-1-(phenylsulfonyl)benz[*f*]indole (Yokum & Fronczek, 1997) and 94.0 (2)° in 1-(phenyl sulfonyl)indole (Beddoes *et al.*, 1986). The sum of the angles around the indole atom N1 is 354.8° indicating sp^2-hybridization.

The value of the O4—N2—C7—C6 torsion angle of −2.6 (4)°, reveals that the nitro group is essentially coplanar with the indole six-membered ring. The sum of the bond angles surrounding atom N2 is 360.0, indicating sp^2-hybridization, and the geometric parameters defining this group are all consistent with those reported for nitrobenzene (Trotter, 1959). No previous X-ray crystal structure determinations have been reported for simple nitroindoles, and the only related examples seem to be 7-nitroindole nucleosides (Kotera *et al.*, 2000), 5-nitroindole (no geometric parameters) (Kang *et al.*, 1997), and 5-nitroindole nucleotides (Loakes *et al.*, 1997).

Experimental

A mixture of compounds (I) and (II) was prepared as described by nitration of 1-(phenylsulfonyl)indole (260 mg, 1.0 mol) with acetyl nitrate (Pelkey & Gribble, 1999). Since the minor 6-nitro isomer, (II), cannot be separated from the major isomer, (I), by flash silica gel chromatography or selective recrystallization, we treated the mixture with ethyl isocyanoacetate (0.11 ml, 1.0 mmol) and 1,5-diaza-bicyclo[5.4.0]undecane (DBU) (0.15 ml, 1.0 mmol) under Barton–Zard reaction conditions, whereby reaction occurs selectively with (I) but not with (II) (Pelkey *et al.*, 1996). Flash chromatography (1:1 CH$_2$Cl$_2$/hexanes) of this reaction product gave (II) as a colorless

amorphous solid, m.p. 470–473 K (lit. m.p. 470 K; Caixach *et al.*, 1979). Crystallization from CH$_2$Cl$_2$/hexane (1:1 *v*/*v*, 10 ml) afforded crystals of (II) suitable for X-ray analysis.

Crystal data

C$_{14}$H$_{10}$N$_2$O$_4$S	$V = 674.93$ (17) Å^3
$M_r = 302.30$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.487$ Mg m^{-3}
$a = 7.8846$ (10) Å	Mo $K\alpha$ radiation
$b = 7.9971$ (16) Å	$\mu = 0.26$ mm^{-1}
$c = 11.5181$ (8) Å	$T = 296$ K
$\alpha = 81.200$ (10)°	Prism, yellow
$\beta = 91.080$ (8)°	$0.60 \times 0.40 \times 0.40$ mm
$\gamma = 109.782$ (10)°	

Data collection

Rigaku AFC-6S diffractometer	1770 reflections with $I > 3\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.013$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{max} = 27.5°$
$T_{min} = 0.861$, $T_{max} = 0.904$	3 standard reflections every 150 reflections intensity decay: 1.2%
3313 measured reflections	
3091 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.29P]$,
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{max} <0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
1770 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
191 parameters	Extinction correction: Larson (1970), equation 22
H-atom parameters constrained	Extinction coefficient: 132 (15)

The H atoms were included in the riding model approximation with C—H = 1.00–1.03 Å, and with U_{iso}(H) = 1.08–1.28U_{eq}(C).

Data collection: *CrystalStructure* (Rigaku/MSC, 2003); cell refinement: *CrystalStructure*; data reduction: *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *CRYSTALS*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CRYSTALS*.

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