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ORIGINAL PAPER

Structures of Three New (Phenylsulfonyl)Indole Derivatives

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Abstract Three new 1-(phenylsulfonyl)indole derivatives, 3-acetyl-2-ethyl-1-(phenylsulfonyl)indole, (I), 2-benzyl-1-(phenylsulfonyl)indole, (II), and 3-trimethylsilylethynyl-1-(phenylsulfonyl)indole, (III), have been synthesized and their crystal structures determined by single crystal X-ray crystallography. (I), $C_{18}H_{17}NO_3S$, is triclinic with space group P-1 and cell constants: $a = 8.6129(2)$ Å, $b = 8.8366(2)$ Å, $c = 11.0108(2)$ Å, $\alpha = 72.7920(1)°$, $\beta = 75.0120(1)°$, $\gamma = 77.2550(1)°$, $V = 763.79(3)$ Å^3 and Z = 2. (II), $C_{21}H_{17}NO_2S$, is monoclinic with space group P21/*n* and cell constants: $a = 10.8355(18)$ Å, $b = 10.6987(19)$ Å, $c = 14.472(3)$ Å, $\beta = 75.0120(1)$, $V = 1675.2(5)$ Å^3 and Z = 4. (III), $C_{19}H_{19}NO_2SSi$, is monoclinic with, space group P21/*c* and cell constants: $a = 12.9596(1)$ Å, $b = 10.543(3)$ Å, $c = 13.543(2)$ Å, $\beta = 93.58°$, $V = 1846.8(6)$Å^3 and $Z = 4$. All three have the same (phenylsulfonyl)indole skeleton with different ligands attached to the 2- and 3-sites of the indole ring. The angle between the mean planes of the indole and benzyl groups is 76.9(6)° (I), 82.9(3)° (II), 89.6(2)° (III) and between the sulfonyl group with the indole and benzyl rings is 61.2(9)° (I), 59.0((5)° (II), 51.5(6)°, 42.5(8)° (III) and 51.5(6)°(I), 44.3(8)° (II), 47.2(8)° (III), respectively. In addition to the ligand substitutions, weak intermolecular C–H···O hydrogen bond interactions and π stacking interactions between the π orbitals of nearby indole and phenyl rings influence these twist angles. Comparison to a MOPAC AM1 computational calculation supports these observations.

Keywords Crystal structure · Hydrogen bonds · Indole · Phenylsulfonyl · *MOPAC* · AM1

Introduction

In connection with our interest in novel indole chemistry [1], we have synthesized three new indole derivatives with the 1-(phenylsulfonyl)indole skeleton and carried out the X-ray structure determination of each of these molecules. Derivatives of 1-(phenylsulfonyl)indole have proven to be remarkably useful in the synthesis of biologically active alkaloids and related analogues, including pyridocarbazoles, such as the anticancer alkaloid ellipticine, carbazoles, furoindoles, pyrroloindoles, indolocarbazoles, and other substituted indoles [1]. Furthermore, we have used 2- and 3-nitro-1-(phenylsulfonyl)indoles in a variety of Diels–Alder reactions, 1,3-dipolar cycloaddition reactions, and nucleophilic addition reactions. The indole phenylsulfonyl moiety is a protecting and activating group *par excellence*.

Experimental

Synthesis of 3-Acetyl-2-Ethyl-1-(Phenylsulfonyl) Indole (I)

The synthesis of (**I**) was performed by stirring aluminum chloride (0.57 g, 4.3 mmol) and acetic anhydride (0.20 mL, 2.1 mmol) in methylene chloride (20 mL) at 273 K (Fig. 1). After 20 min a solution of 2-ethyl-1-(phenylsulfonyl)indole (0.19 g, 0.67 mmol) in methylene

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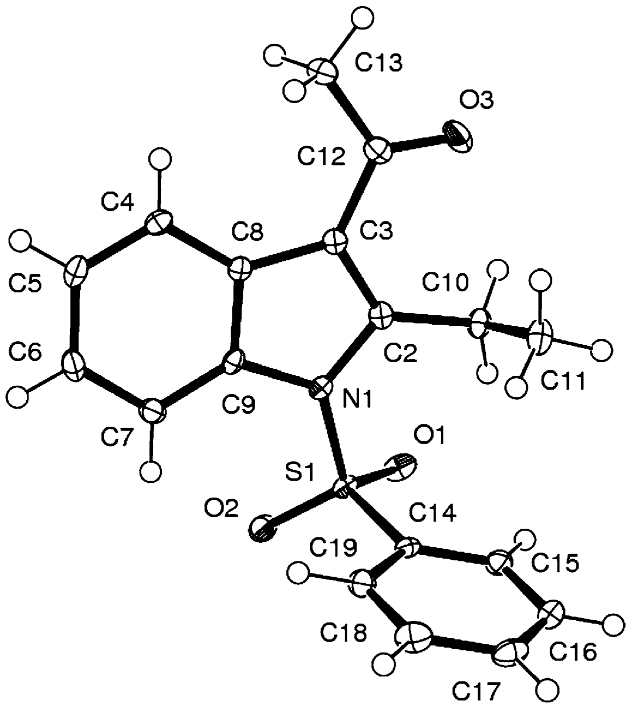


Fig. 1 ORTEP drawing of $C_{18}H_{17}NO_3S$, (**I**), showing the atom numbering scheme and 50% probability displacement ellipsoids

chloride (3.5 mL) was added to the yellow suspension via addition funnel. The solution was stirred for 2.5 h at 273 K, after which it was poured over crushed ice (~100 mL). The organic layer was extracted with methylene chloride (3 × 20 mL). The combined organic extracts were washed with brine (2 × 25 mL) and saturated aqueous sodium bicarbonate (25 mL), and were dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo, yielding brown oil, which was stored at 277 K. White crystals suitable for X-ray diffraction studies were obtained after vacuum filtration (0.14 g, 0.44 mmol, 65%): mp 344–346 K; ^{1}H NMR ($CDCl_3$) δ 8.30–8.28 (m, 1H), 7.90–7.88 (m, 1H), 7.81 (d, 2H, J = 8.5 Hz), 7.59 (t, 1H, J = 7.5 Hz), 7.47 (t, 2H, J = 7.5 Hz), 7.37–7.33 (m, 2H), 3.38 (q, 2H, J = 7.5 Hz), 2.66 (s, 3H), 1.37 (t, 3H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ195.9, 149.7, 139.2, 136.3, 134.5, 129.8 (2C), 127.4, 126.7 (2C), 125.0, 124.7, 121.0, 120.5, 115.2, 32.3, 21.1, 15.6; IR ν(TCE) 3,394, 2,978, 2,471, 1,884, 1,801, 1,672, 1,533, 1,448, 1,385, 1,224, 1,182, 1,122, 1,093, 1,056 cm^{-1}.

Synthesis of 2-Benzyl-1-(Phenylsulfonyl)Indole (II)

The synthesis of (**II**) was performed by adding *sec*-butyllithium (1.4 M, 5.8 mL, 8.1 mmol) dropwise via syringe to a solution of 1-(phenylsulfonyl)indole (1.4 g, 5.4 mmol) in anhydrous THF (30 mL) at 195 K (Fig. 1). After 5 h benzyl bromide (0.64 mL, 5.4 mmol) was added quickly via syringe at 195 K. The reaction mixture was allowed to warm up to room temperature. It was poured onto saturated aqueous ammonium chloride (50 mL). The organic layer was extracted with diethyl ether (3 × 50 mL), washed with brine (2 × 50 mL), and dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo, yielding a dark-brown oil. The oil was purified via column chromatography (1:1 hexanes: ethyl acetate). A tan-colored solid (1.5 g, 4.4 mmol, 81%) was obtained: mp 371–373 K; ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 1H, J = 8.7 Hz), 7.66 (d, 2H, J = 8.4 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.38 (d, 3H, J = 8.1 Hz), 7.34 (s, 1H), 7.31–7.26 (m, 3H), 7.22 (d, 3H, J = 8.1 Hz), 6.13 (s, 1H), 4.37 (s, 2H); MS *m/z* 347, 205, 178, 128, 77.

Synthesis of 1-(Phenylsulfonyl)-3-Trimethylsilylethynyl-Indole (III)

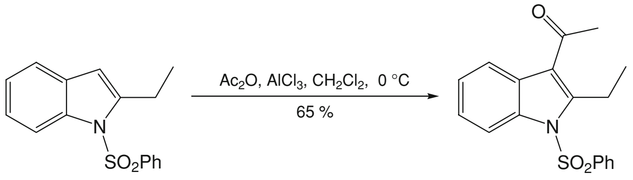
The synthesis of (**III**) was performed by stirring 3-iodo-1-(phenylsulfonyl)indole (0.225 g, 0.588 mmol), copper iodide (0.0050 g, 0.026 mmol), and (trimethylsilyl)acetylene (0.1 mL, 0.7 mmol) in triethylamine. The reaction mixture was degassed and tetrakis(triphenylphosphine) palladium was added quickly. The reaction mixture was stirred overnight. Diethyl ether (25 mL) and 2 M HCl (25 mL) were added to the yellowish reaction mixture. The organic layer was extracted with diethyl ether (3 × 25 mL), washed with brine (2 × 30 mL), and dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo, yielding a brown oil, which was purified via column chromatography (1:1 hexanes: methylene chloride). Colorless crystals were obtained (0.0934 g, 0.264 mmol, 45%): mp 385–385.5 K; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 1H, J = 7.5 Hz), 7.90 (d, 2H, J = 7.5 Hz), 7.78 (s, 1H), 7.65 (d, 1H, J = 7.8 Hz), 7.56 (t, 1H, J = 7.8 Hz), 7.45 (t, 2H, J = 6.6 Hz), 7.40–7.28 (m, 2H), 0.29 (s, 9H); MS *m/z* 353 (M+), 338, 212 (100%), 196, 168, 77.

Structure Determination and Refinement

X-ray data were collected with a Bruker Apex II CCD area detector [2] using graphite-monochromated Cu–Kα (λ = 1.54178 Å) at 100(2) K for (**I**) and Mo–Kα (λ = 0.71073 Å) at 93(2)K for (**II**) and (**III**). The structure was solved by direct methods using SHELXS97 [3]. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97 [3]. All H atoms were placed in their calculated positions and included in the refinement using the riding model. An absorption correction was performed on (**I**) and (**II**) using SADABS [4] and all calculations were performed using SHELXTL [2]. Each structure was checked using PLATON [5]. Crystal and experimental data for (**I**), (**II**), and (**III**) is listed in Table 1. Schemes 1, 2 and 3 show the molecular structures of (**I**), (**II**) and (**III**), respectively. Ortep diagrams [6] of the asymmetric unit and crystal packing of (**I**), (**II**), and (**III**) are displayed in Figs. 1, 2, 3, 4, 5 and 6, respectively. The short C(16)–C(17) triple bond in (**III**) is in the range of a normal triple bond. Bond lengths and bond angles for each structure are all within expected ranges [7]. Selected geometric parameters for (**I**), (**II**), and (**III**) are listed in Table 2.

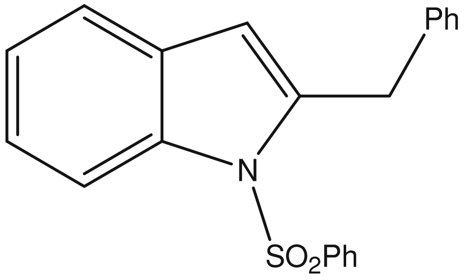
Results and Discussion

The dihedral angles between the mean planes of the indole ring and the benzene ring of the phenylsulfonyl group are 76.9(6)° (**I**), 82.9(3)° (**II**), 89.6(2)° (**III**). The dihedral angle in (**I**) is much lower than the 80–90° typically observed (e.g. 86.80(6)° [8], 82.83(5)° [9], 85.6(1)° [10] and 90.2(2)° and 94.0(2)° [11]) and closer to the 66.2(4)° observed by Liu et al. [12] which presumably reflects interaction of the ethyl group at C2 (Fig. 1).



II

Scheme 1 Synthesis of **I**

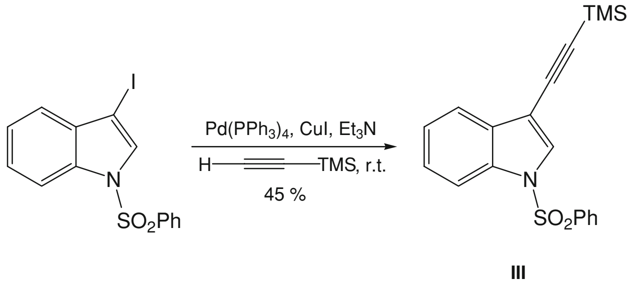


II

Scheme 2 Chemical structure of **II**

Table 1 Crystal and Experimental Data for (**I**), (**II**) and (**III**)

	(I)	(II)	(III)
Formula	$C_{18}H_{17}NO_3S$	$C_{21}H_{17}NO_2S$	$C_{19}H_{19}NO_2SSi$
Formula weight	327.39	347.42	353.50
Crystal color, habit	Colorless, block	Colorless, needle	Colorless, needle
Crystal size (mm)	0.29 × 0.28 × 0.25	0.90 × 0.35 × 0.20	0.70 × 0.45 × 0.35
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group, Z	P − 1, 2	P 21/*n*, 4	P 21/*c*, 4
Temperature (K)	100(2)	93(2)	93(2)
a (Å)	8.6129(2)	10.8355(18)	12.9596(10)
b (Å)	8.8366(2)	10.6987(19)	10.543(3)
c (Å)	11.0108(2)	14.472(3)	13.543(2)
α (°)	72.7920(1)	90.000(0)	90.000(0)
β (°)	75.0120(1)	93.123(3)	93.5(8)
γ (°)	77.2550(1)	90.000(0)	90.000(0)
Volume, $Å^3$	763.79(3)	1,675.2(5)	1,846.8(6)
F(000)	344	728	744
Absorption coeff (mm^{-1})	2.012	0.207	0.251
D_{calc} ($Mg\ m^{-3}$)	1.424	1.378	1.271
No. of reflections	2,414	4,062	4,562
$2\theta_{max}$/° with Cu K_a/Mo K_a	130.2	56.6	56.5
R, R_w [$I > 2\sigma(I)$]	0.0332/0.0864	0.0382/0.0920	0.0514/0.1167
$(\Delta\rho)_{max/min}/e\ Å^{-3}$	0.69/−0.35	0.311/−0.463	0.466/−0.563
GOF on F^2	1.065	1.039	0.889
Measurement		APEX2 [2]	
Program system		SHELXTL	
Structure determination		SHELXS97	
Refinement	Full-matrix least-squares on F^2 (SHELXL97)		



Scheme 3 Synthesis of **III**

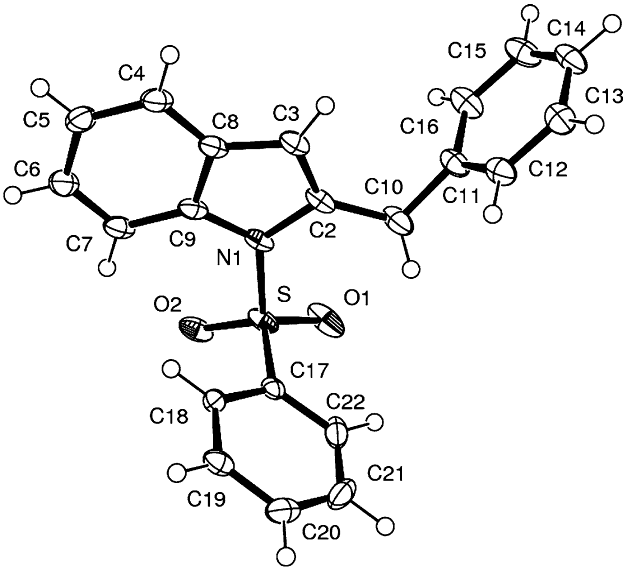


Fig. 2 ORTEP drawing of $C_{21}H_{17}NO_2S$, (**II**), showing the atom numbering scheme and 50% probability displacement ellipsoids

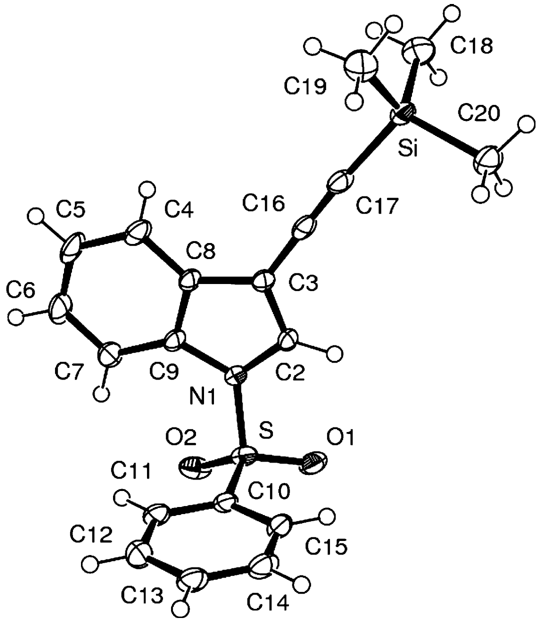


Fig. 3 ORTEP drawing of $C_{19}H_{19}NO_2SSi$, (**III**), showing the atom numbering scheme and 50% probability displacement ellipsoids

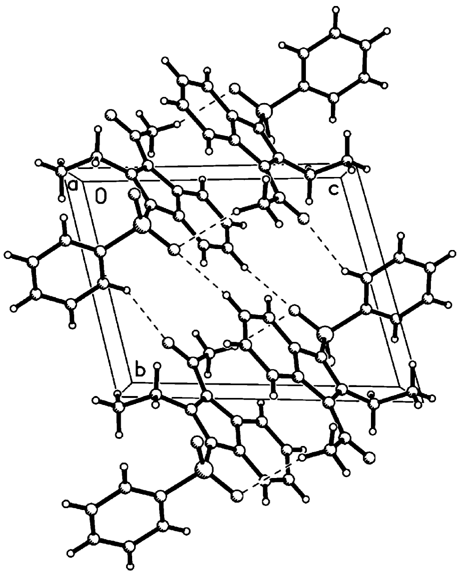


Fig. 4 The molecular packing for (**I**) viewed down the *a* axis. *Dashed lines* indicate weak C–H···O intermolecular hydrogen bond interactions

The sulfonyl group in (**I**), (**II**), and (**III**) adopts the usual nitrogen-sulfonyl geometry seen with other 1-(phenylsulfonyl)indoles wherein the N lone pair eclipses the sulfonyl group [13]. Accordingly, the O1–S1–N1–C2 torsion angles in (**I**), (**II**), and (**III**) are −38.8(15)°, −39.12(14)° and −33.20(15)°. For comparison, the O1–S1–N1–C2 torsion angle in 1-(phenylsulfonyl)indole is −37° and that in (phenylsulfonyl)pyrrole is −35° [14]. The benzene ring of the phenyl group at C2 in (**II**) is twisted by an angle of 68.4(8)° which would allow for minimal interaction with the phenylsulfonyl group and thereby supporting its higher torsion angle value (Fig. 2). The value of the twist angle between the sulfonyl group with the indole and phenyl rings is 61.2(9)° (**I**), 59.0(5)° (**II**), 42.5(8)° (**III**) and 51.5(6)°(**I**), 44.3(8)° (**II**), 47.2(8)° (**III**), respectively, which actively supports the premise that a decrease in the twist angle between the sulfonyl group and indole ring is heavily influenced by the nature and bulk of the substituent attached at C2. In (**I**) the separation between H10B with O1 measures 2.22(9) Å while in (**II**) the separation between H10 and O1 is 2.35(5) Å and the separation of H2A and O1 in (**III**) is 2.59(6) Å. There is no substituent attached to C2 in (**III**) (Fig. 3). Clearly, the proximity and bulk of the substituent at C2 is a major influence in the value of this twist angle. This along with crystalline packing effects described below play a key role in the structural relationships of the various groups on the geometry of the molecular structures in (**I**), (**II**), and (**III**) (Fig. 2).

The sum of the angles around the indole N atom is 359.9(6)° (**I**), 357.8(6)° (**II**) and 356.4(4)° (**III**), indicating

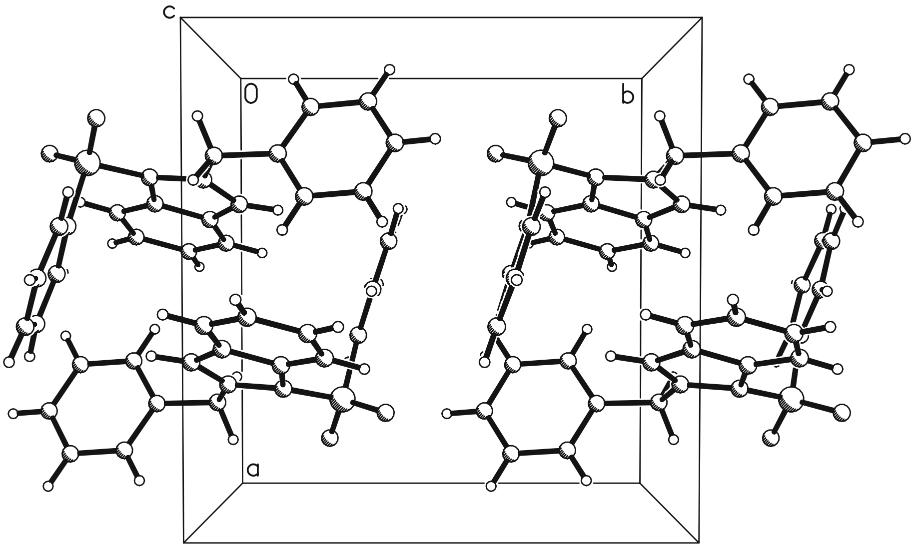


Fig. 5 The molecular packing for (**II**) viewed down the *c* axis

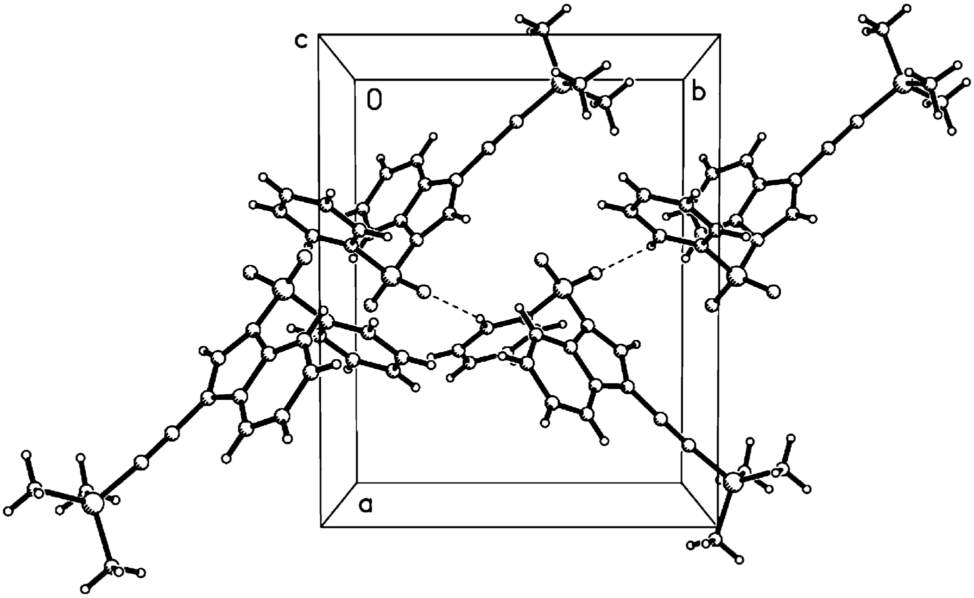


Fig. 6 The molecular packing for (**III**) viewed down the *c* axis. *Dashed lines* indicate weak C–H···O intermolecular hydrogen bond interactions

nearly ideal sp^2 hybridization in each compound. The C2=C3 indole double-bond length is 1.375(3) Å (**I**), 1.350(2) Å (**II**) and 1.346(2) Å (**III**) which is longer in (**I**) but similar in (**II**) and (**III**) to indole double-bond lengths of 1.349(11) Å [14] and 1.355(5) Å [12] observed in similarly related indole compounds. All of the other geometric parameters are within expected ranges [7]. In (**I**) there are weak intermolecular C–H···O hydrogen bond interactions between an oxygen atom (O2) from the sulfonyl group and hydrogen atoms from a nearby indole ring (H6) and a 4-acetyl group (H13) as well as from an oxygen atom (O3) from the acetyl group and a hydrogen atom (H19) from a phenyl group (Table 3) which help link the molecules into chains along the 011 plane of the unit cell (Fig. 4). No intermolecular hydrogen bonds are evident in (**II**) (Fig. 5). Weak intermolecular hydrogen bonds in (**III**) occur between the sulfonyl oxygen O1 and H11 from the phenyl ring which help link the molecules into chains along the 110 plane of the unit cell (Fig. 6).

Additional packing interactions are observed in the crystalline environments of molecules (**I**) and (**II**) only. In (**I**) intermolecular π stacking interactions occur between Cg1/Cg1, Cg1/Cg2 and Cg3/Cg3-π orbitals of nearby indole rings [Cg1···Cg1 = 3.9092(10) Å $(-x, -y, 1 - z)$; Cg1···Cg2 = 3.5706(1) Å $(-x, -y, 1 - z)$; Cg3···Cg3 = 3.8373(1) Å $(1 - x, 1 - y, -z)$; where Cg1 (N1–C2–C3–C8–C9), Cg2 (C4–C9) and Cg3 (C14–C19) = center of gravity of the two groups within the indole ring and the phenyl group, respectively]. In (**II**) there are weak intermolecular C–H···Cg packing interactions between the Cg2-π

Table 2 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for (**I**), (**II**) and (**III**)

(**I**) $C_{18}H_{17}NO_3S$			
S(1)–O(1)	1.4287(14)	S(1)–O(2)	1.4206(13)
S(1)–N(1)	1.6941(14)	S(1)–C(14)	1.7578(17)
N(1)–C(2)	1.404(2)	N(1)–C(9)	1.423(2)
C(2)–C(3)	1.375(2)	C(12)–O(3)	1.220(2)
(**II**) $C_{21}H_{17}NO_2S$			
S–O(1)	1.4271(12)	S–O(2)	1.4238(12)
S–N(1)	1.6618(13)	S–C(17)	1.7564(15)
N(1)–C(2)	1.4291(19)	N(1)–C(9)	1.419(2)
C(2)–C(3)	1.350(2)	C(2)–C(10)	1.496(2)
(**III**) $C_{19}H_{19}NO_2SSi$			
S–O(1)	1.4174(13)	S–O(2)	1.4120(13)
S–N(1)	1.6555(15)	S–C(10)	1.7412(18)
Si–C(17)	1.826(2)	Si–C(18)	1.842(2)
Si–C(19)	1.840(2)	Si–C(20)	1.843(2)
N(1)–C(2)	1.382(2)	N(1)–C(9)	1.404(2)
C(2)–C(3)	1.346(3)	C(3)–C(16)	1.419(3)
C(16)–C(17	1.197(2)	C(3)–C(8)	1.445(2)
(**I**) $C_{18}H_{17}NO_3S$			
O(1)–S(1)–O(2)	119.17(7)	O(1)–S(1)–N(1)	107.88(7)
O(1)–S(1)–C(14)	109.64(8)	O(2)–S(1)–N(1)	105.45(7)
O(2)–S(1)–C(14)	109.74(8)	N(1)–S(1)–C(14)	103.77(7)
S(1)–N(1)–C(2)	125.45(11)	S(1)–N(1)–C(9)	125.42(11)
C(2)–N(1)–C(9)	109.05(13)	N(1)–C(2)–C(3)	108.52(14)
C(3)–C(12)–C(3)	121.38(16)	O(3)–C(12)–C(13)	119.30(16)
S(1)–C(14)–C(15)	119.54(13)	S(1)–C(14)–C(19)	118.30(15)
(**II**) $C_{21}H_{17}NO_2S$			
O(1)–S–O(2)	119.53(7)	O(1)–S(1)–N(1)	107.57(7)
O(1)–S–C(17)	108.54(8)	O(2)–S–N(1)	105.74(7)
O(2)–S–C(17)	109.06(6)	N(1)–S–C(17)	105.51(6)
S–N(1)–C(2)	125.49(11)	S–N(1)–C(9)	124.17(10)
C(2)–N(1)–C(9)	108.05(12)	N(1)–C(2)–C(3)	108.23(14)
S–C(17)–C(22)	119.54(12)	S–C(17)–C(18)	118.91(11)
(**III**) $C_{19}H_{19}NO_2SSi$			
O(1)–S–O(2)	120.65(8)	O(1)–S–N(1)	104.76(8)
O(1)–S–C(10)	109.66(9)	O(2)–S–N(1)	106.24(8)
O(2)–S–C(10)	109.73(8)	N(1)–S–C(10)	104.42(8)
S–N(1)–C(2)	121.41(12)	S–N(1)–C(9)	126.80(12)
C(2)–N(1)–C(9)	108.23(14)	N(1)–C(2)–C(3)	110.16(16)
S–C(10)–C(15)	119.52(15)	S–C(10)–C(11)	118.57(14)
(**I**) $C_{18}H_{17}NO_3S$			
O(1)–S(1)–N(1)–C(2)	−38.8(15)	O(1)–S(1)–N(1)–C(9)	137.43(14)
O(1)–S(1)–C(14)–C(15)	4.31(16)	O(1)–S(1)–C(14)–C(19)	−174.20(12)
O(2)–S(1)–N(1)–C(2)	−167.24(13)	O(2)–S(1)–N(1)–C(9)	9.07(15)

Table 2 continued

(I) $C_{18}H_{17}NO_3S$			
O(2)–S(1)–C(14)–C(15)	136.98(13)	O(2)–S(1)–C(14)–C(19)	−41.52(15)
C(14)–S(1)–N(1)–C(2)	77.39(15)	C(14)–S(1)–N(1)–C(9)	−106.30(14)
N(1)–S(1)–C(14)–C(15)	−110.73(14)	N(1)–S(1)–C(14)–C(19)	70.77(14)
S(1)–N(1)–C(2)–C(3)	175.42(11)	S(1)–N(1)–C(2)–C(10)	−8.9(2)
N(1)–C(2)–C(3)–C(8)	0.17(18)	N(1)–C(2)–C(3)–C(12)	−179.89(14)
C(2)–C(3)–C(12)–O(3)	3.9(3)	C(8)–C(3)–C(12)–O(3)	−176.21(16)
(II) $C_{21}H_{17}NO_2S$			
O(1)–S–N(1)–C(2)	−39.12(14)	O(1)–S–N(1)–C(9)	160.15(12)
O(1)–S–C(17)–C(18	−179.7 3(11)	O(1)–S–C(17)–C(22)	−3.7(14)
O(2)–S–N(1)–C(2)	−167.90(11)	O(2)–S–N(1)–C(9)	31.37(13)
O(2)–S–C(17)–C(18)	−47.19(13)	O(2)–S–C(17)–C(22)	128.49(12)
C(17)–S–N(1)–C(2)	76.61(13)	C(17)–S–N(1)–C(9)	−84.13(12)
N(1)–S–C(17)–C(18)	65.21(13)	N(1)–S(1)–C(17)–C(22)	−118.32(12)
S–N(1)–C(2)–C(3)	−165.94(10)	S–N(1)–C(2)–C(10)	14.7(2)
N(1)–C(2)–C(3)–C(8)	1.77(16)	N(1)–C(2)–C(10)–C(11)	170.00(13)
(III) $C_{19}H_{19}NO_2SSi$			
O(1)–S–N(1)–C(2)	−33.20(15)	O(1)–S–N(1)–C(9)	170.64(14)
O(1)–S–C(10)–C(11)	−165.97(14)	O(1)–S–C(10)–C(15)	15.02(18)
O(2)–S–N(1)–C(2)	−161.94(12)	O(2)–S–N(1)–C(9)	41.91(16)
O(2)–S–C(10)–C(11)	−31.27(17)	O(2)–S–C(10)–C(15)	149.72(15)
C(10)–S–N(1)–C(2)	82.08(14)	C(10)–S–N(1)–C(9)	−74.07(16)
N(1)–S–C(10)–C(11)	82.25(16)	N(1)–S(1)–C(10)–C(15)	−96.77(16)
S–N(1)–C(2)–C(3)	−162.55(12)	S–N(1)–C(9)–C(7)	−21.6(3)
N(1)–C(2)–C(3)–C(8)	1.58(19)	N(1)–C(2)–C(3)–C(16)	−176.80(15)

Table 3 Weak hydrogen bond interactions for (**I**) and (**III**) (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
(I)				
C6–H6–O2#1	0.95	2.49	3.404(2)	160.3
C13–H13C–O2#2	0.98	2.56	3.514(2)	164.5
C19–H19–O3#3	0.95	2.39	3.156(2)	137.4
(III)				
C11–H11A–O1#4	0.95	2.48	3.333(2)	149.4

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $1-y$, $1-z$; #2 $-x$, $-y$, $1-z$; #3 x, $1+y$, z; #4 $1-x$, $1/2+y$, $1/2-z$

orbitals of the indole [Cg2=C4–C9] and phenyl rings, Cg3 [Cg3=C11–C16], and hydrogen atoms from the benzyl ring [C19–H19A···Cg3^{i}; C22–H22A···Cg3^{iii} and C20–H20A···Cg2^{ii}] and between Cg2-π orbitals of the indole ring and a hydrogen atom from the benzyl ring, [C12–H12A···Cg2^{i}], respectively (Fig. 3). [C12–H12A···Cg2 = 3.5305(18) Å; C19–H19A···Cg3 = 3.6437(19) Å; C20–H20A···Cg2 = 3.359(2) Å; C22–H22A···Cg3 = 3.5833(19) Å; Cg2 & Cg3 = center of gravity of C4–C9; and C11–C16, respectively; i = $1-x$, $-y$, $1-z$; ii = $-1/2-x$, $1/2-y$, $-1/2+z$; iii = $3/2-x$, $1/2+y$, $1/2-z$]. In (**III**) the closest intermolecular distance between rings occurs with Cg1/Cg3 [Cg1···Cg3 = 4.4482(17) Å (x, y, z] which is too long for any appreciable π orbital interaction.

MOPAC calculations were performed on (**I**) and (**II**) with *MOPAC* as implemented by *WeMO Pro* [15]. Compound (**III**) would not converge with either AM1, PM3 or MNDO. The AM1 (Austin Model 1) approximation together with the Hartree-Fock closed-shell (restricted) wavefunction was used for (**I**) and (**II**) and minimizations were teminnated at an r.m.s. gradient of less than 0.01 kJ mol^{-1} Å^{-1}. When the refined atom coordinates in (**I**) are subjected to a *MOPAC* calculation the angle between the mean planes of the indole and benzyl ring becomes 78.6(9)° and the angle between the sulfonyl group and the mean planes of the indole and benzyl rings are 49.6(5)° and 55.4(4)°, respectively. The increase of nearly 2° in the angles between the indole and benzyl rings in (**I**) coincides with the decrease and increase in values of nearly 4° for the angles between the sulfonyl group with the indole and benzyl rings, respectively. It is clear that weak hydrogen bonding and π-ring interactions influence this twist angle value for the various groups within the molecule in this crystal.

When the refined atom coordinates in (**II**) are subjected to a *MOPAC* calculation the angle between the mean planes of the indole and the benzyl ring becomes 82.9(3)° and the angle between the sulfonyl group and the mean planes of the indole and benzyl rings are 48.0(9)° and 54.4(2)°, respectively. The increase of just over 2° in the angles between the indole and benzyl rings in (**II**) also coincides with the decrease and increase in values of close to 4° for the angles between the sulfonyl group with the indole and benzyl rings, respectively. In relating these values to those in the crystals themselves outlined earlier, it is clear that the weak hydrogen bonding interactions, Cg···Cg interactions and intermolecular C–H···Cg packing interactions all have a significant influence in concert on the twist angle values for the comparitive groups in these molecules.

Supporting Information Available

X-ray crystallographic files, in Cif format, for the structure determinations of (**I**) (695250), (**II**) (695251) and (**III**) (695252) have been deposited with the Cambridge Crystallographic Date Center, CCDC: 26091. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033; email: deposit@ccdc.cam.uk or at www: http://www.ccdc.cam.ac.uk).

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