

N,N-Dimethyl-1-phenylsulfonyl-1*H*-pyrrole-3-sulfonamide

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The structure of the title compound, C₁₂H₁₄N₂O₄S₂, has been determined as part of an investigation into the structure and substitution patterns in benzenesulfonyl-protected pyrroles. The pyrrole N atom is in a near-planar bonding environment, with an angle between the S–N bond and the mean plane of the pyrrole ring of 1.72 (10)°.

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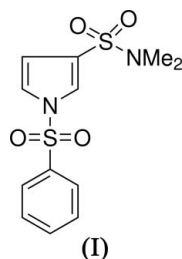
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ (C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.109
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

In contrast with the expected 'normal' C-2 substitution of pyrroles, it has recently been shown that the sulfonation of pyrrole using a sulfur trioxide–pyridine complex produced 3-sulfonated derivatives (Mizuno *et al.*, 2000). Whether such C-3 regioselectivity is due to direct sulfonation at that site or *via* rearrangement of an initially produced C-2 isomer remains to be elucidated. However, it has been recognized for some time that 2-pyrrolylsulfides, -sulfoxides and -sulfones and sulfinylpyrroles (DeSales *et al.*, 1982; Kakushima & Frenette, 1984; Carmona *et al.*, 1980) have a pronounced tendency to undergo acid-mediated inter- and/or intramolecular rearrangement to the C-3 isomer. Aware of such possibilities, we have initiated a study of the sulfonylation reactions of 1-(benzenesulfonyl)pyrroles.

Since rare-earth catalysts have shown promise in both Friedel–Crafts acylation and sulfonylation reactions of aromatics (Le Roux & Dubac, 2002), we chose to explore the use of such catalysts for this purpose. For the sulfamoylation of 1-(benzenesulfonyl)pyrrole with dimethylsulfamoyl chloride, a set of multiparallel reactions was assembled utilizing bismuth(III) trifluoromethanesulfonate, indium(III) trifluoromethanesulfonate, scandium(III) trifluoromethanesulfonate and ytterbium(III) trifluoromethanesulfonate as catalysts, in nitromethane and dichloroethane (DCE) as solvents. While Yb(OTf)₃ and Sc(OTf)₃ were found to be ineffective, both In(OTf)₃ and Bi(OTf)₃ catalysts were capable of effecting the desired sulfamoylation, yielding the title compound, (I), the subject of this paper.



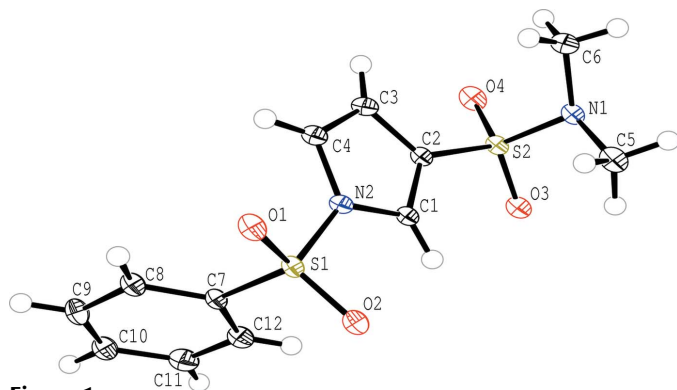


Figure 1

A view of (I), showing the atom-numbering scheme and with displacement ellipsoids drawn the 50% probability level.

are mindful of the statement by Muchowski: 'The formation and rearrangement of 2-substituted pyrroles can take place at comparable rates. Therefore, mechanistic conclusions based on product distributions obtained in the electrophilic substitution of pyrroles should be made with circumspection in the absence of kinetic information on the ratios of the products. This is a precaution that in many examples reported in the literature has not been taken. It would, therefore, seem worthwhile to re-examine the electrophilic substitution of pyrroles in general with this point in mind.' (DeSales *et al.*, 1982).

The central five-membered ring in the molecule of (I) is completely planar (maximum deviation 0.006 Å), with the benzenesulfonyl and *N,N*-dimethylsulfonamide groups in an anti orientation across the central pyrrole ring. The angle between the S1–N1 bond and the pyrrole ring plane is 1.72 (10)°, which implies that the pyrrole N atom is *sp*²-hybridized, consistent with an aromatic pyrrole ring. The sulfonamide N atom has bond angles consistent with *sp*³-hybridized orbitals, as would be expected.

Bond distances and angles within the structure are within expected ranges of values (Cambridge Structural Database, Version 5.27; Allen, 2002).

Experimental

To a mixture of *N*-(benzenesulfonyl)pyrrole (4.8 mmol, 1.0 g) and bismuth(III) trifluoromethanesulfonate (0.69 mmol, 0.63 g) in 1,2-dichloroethane (20 ml) was added dimethylsulfamoyl chloride (4.8 mmol, 0.69 g). The reaction was stirred in a closed reaction vessel at 328 K for 20 h. The reaction mixture was diluted with water and extracted with dichloromethane. The combined organic extracts were washed with 3 M HCl, saturated aqueous NaHCO₃ and brine, dried with Na₂SO₄, and concentrated at reduced pressure. The resulting crude oil was submitted to flash chromatography [hexanes–dichloromethane, 70:30 (400 ml), linear ramp to 0:100 (300 ml)] to afford 0.31 g (49%) of pure (I) (m.p. 390–393 K). The isolated compound was recrystallized from methanol to yield crystals of a size and quality suitable for X-ray diffraction. Analysis, calculated for C₁₂H₁₄N₂O₄S₂: C 45.85, H 4.49, N 8.91, S 20.40%; found: C 45.79, H 4.50, N 8.71, S 20.70%. ¹³C NMR (300 MHz, CDCl₃, δ, p.p.m.): 137.7, 134.9, 129.9, 127.3, 123.6, 123.3, 121.9, 112.0, 37.8. GC/MS EIMS *m/e*: 314 (M⁺), 77 (100).

Crystal data

C₁₂H₁₄N₂O₄S₂
M_r = 314.37
 Monoclinic, *P*2₁/*n*
a = 8.1322 (7) Å
b = 11.1027 (9) Å
c = 16.0757 (14) Å
 β = 100.680 (2)°
V = 1426.3 (2) Å³
Z = 4

D_x = 1.464 Mg m⁻³
 Mo K α radiation
 Cell parameters from 5103 reflections
 θ = 2.2–28.3°
 μ = 0.39 mm⁻¹
T = 173 (2) K
 Block, colourless
 0.26 × 0.22 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS in S_{AINT-Plus}; Bruker, 2003)
T_{min} = 0.754, *T_{max}* = 0.92

15246 measured reflections
 3534 independent reflections
 3357 reflections with *I* > 2 σ (*I*)
R_{int} = 0.029
 θ_{max} = 28.3°
h = -10 → 10
k = -14 → 14
l = -21 → 21

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.047
wR [*F*²] = 0.109
S = 1.20
 3534 reflections
 237 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.2568P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.30 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–O1	1.4243 (15)	N1–C2	1.378 (2)
S1–O2	1.4255 (14)	N1–C5	1.391 (2)
S1–N1	1.6775 (16)	N2–C7	1.470 (3)
S1–C8	1.7524 (19)	N2–C6	1.473 (3)
S2–O4	1.4318 (15)	C3–C2	1.366 (3)
S2–O3	1.4335 (15)	C3–C4	1.428 (3)
S2–N2	1.6309 (17)	C5–C4	1.351 (3)
S2–C3	1.7409 (19)		
O1–S1–O2	121.63 (9)	C5–N1–S1	124.53 (14)
O1–S1–N1	105.21 (8)	C7–N2–C6	112.49 (18)
O2–S1–N1	105.07 (8)	C7–N2–S2	115.50 (14)
O1–S1–C8	109.24 (9)	C6–N2–S2	115.69 (14)
O2–S1–C8	109.51 (9)	C9–C8–C13	122.18 (18)
N1–S1–C8	104.77 (9)	C9–C8–S1	118.52 (15)
O4–S2–O3	119.76 (9)	C13–C8–S1	119.28 (15)
O4–S2–N2	107.45 (9)	C2–C3–C4	108.83 (17)
O3–S2–N2	106.59 (9)	C2–C3–S2	124.14 (15)
O4–S2–C3	107.21 (9)	C4–C3–S2	126.88 (15)
O3–S2–C3	107.34 (9)	C4–C5–N1	107.72 (17)
N2–S2–C3	108.03 (9)	C3–C2–N1	106.29 (16)
C2–N1–C5	109.96 (16)	C5–C4–C3	107.18 (17)
C2–N1–S1	125.42 (13)		

H atoms were located in a difference-electron density map and refined with isotropic displacement parameters.

Data collection: SMART (Bruker, 2002); cell refinement: S_{AINT-Plus} (Bruker, 2003); data reduction: S_{AINT-Plus}; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEX (McArdle, 1995); software used to prepare material for publication: OSCAIL (McArdle, 1995) and PLATON (Spek, 2003).

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