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N-(1-Benzenesulfonyl-4-acetylpyrrol-3-yl)acetamide

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The structure of the title compound, $C_{14}H_{14}N_2O_4S$, has been determined as part of an investigation into the structure and substitution patterns in benzenesulfonyl-protected pyrroles.

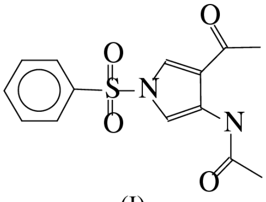
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.182
Data-to-parameter ratio = 22.5

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

Comment

Pyrrole readily undergoes electrophilic substitution in solution, leading to α-substitution. Because pyrrole is a π-electron-rich molecule, in many cases, the reaction does not stop with mono-substitution, but continues, to give higher substitutions. One means of controlling the reactivity of pyrrole is to add a blocking group to the pyrrole ring. While it is possible to attach the blocking group to the α-carbon, it is easier to utilize the N atom. Attachment of an electron-withdrawing group to the N atom attenuates the reactivity and provides a degree of regioselective control. When using benzenesulfonyl as the protecting group, the regiospecificity is found to be controlled by the hardness of the Lewis acid reaction promoter.



(I)

The title compound, (I), was prepared in several steps from 1-benzenesulfonylpyrrole by an initial regioselective acylation to afford 3-acetyl-1-benzenesulfonylpyrrole (Xu *et al.*, 1981; Rokach *et al.*, 1981; Kakushima *et al.*, 1983). Subsequent formation of the corresponding oxime of this ketone followed by Beckmann rearrangement in polyphosphoric acid at 358 K afforded the 3-pyrrolylacetamide (m.p. 443–445 K) as the predominant rearrangement product. Friedel–Crafts acylation using acetic anhydride in the presence of aluminium chloride at 273 K was found to occur regioselectively at the adjacent β site to afford the title 3,4-disubstituted pyrrole (m.p. 424–425 K). Although substitution at the C-4 position of a 3-substituted pyrrole is quite unusual in the absence of a bulky *N*-substituent, Huckel MO calculations upon 1-benzenesulfonylpyrrole-3-ylacetamide indicate that the C-4 position in this C-3 amino-substituted pyrrole is the most electron-rich site of the pyrrole ring (Dewar *et al.*, 1985; Stewart, 1985), suggesting that electrophilic attack should therefore take place at this site. At present, however, it is not clear if the 3,4-

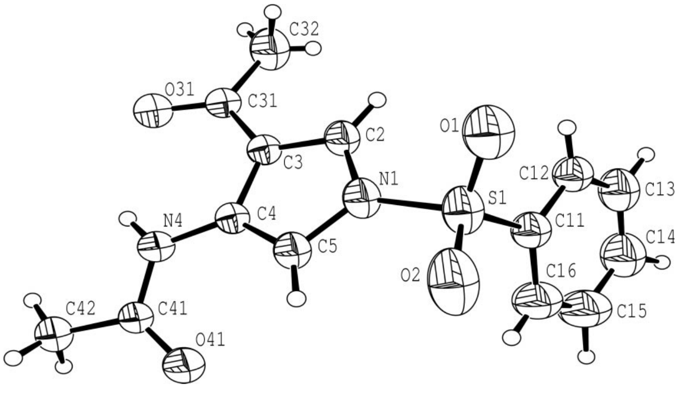


Figure 1
The molecular structure of (I). The ellipsoids represent displacement parameters at the 40% probability level.

disubstitution pattern obtained in this instance is the result of direct acylation at the C-4 site, or the result of an acyl group migration from a kinetically formed isomer. Numerous examples of rearrangement processes of pyrroles have been reported by Kakushima & Frenette (1984), Carmona *et al.* (1980), Carson & Davis (1981) and Xiao *et al.* (1996).

The pyrrole and phenyl ring systems found in the title compound are themselves planar, but they are not coplanar. Considering the pyrrole and phenyl rings of the benzenesulfonylpyrrole and the tetrahedral geometry of the S atom, this is not unexpected.

Experimental

See above for synthesis details.

Crystal data

$C_{14}H_{14}N_2O_4S$
$M_r = 306.34$
Monoclinic, $P2_1/c$
$a = 8.683$ (3) Å
$b = 15.159$ (6) Å
$c = 11.151$ (3) Å
$\beta = 91.06$ (3)°
$V = 1467.5$ (9) Å^3
$Z = 4$
$D_x = 1.387$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.7$–13.9°
$\mu = 0.24$ mm^{-1}
$T = 298$ (2) K
Rectangular, colorless
0.50 × 0.50 × 0.40 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
4709 measured reflections
4277 independent reflections
3261 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 30.0°$
$h = -12 \rightarrow 12$
$k = -1 \rightarrow 21$
$l = -4 \rightarrow 15$
2 standard reflections
frequency: 120 min
intensity decay: 2.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.182$
$S = 1.08$
4277 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1082P)^2 + 0.1541P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4255 (18)	C3—C4	1.439 (2)
S1—O1	1.4277 (19)	C3—C31	1.468 (2)
S1—N1	1.6854 (15)	C4—C5	1.363 (2)
S1—C11	1.751 (2)	C11—C12	1.380 (3)
N1—C2	1.372 (2)	C11—C16	1.387 (3)
N1—C5	1.399 (2)	C12—C13	1.390 (3)
O31—C31	1.218 (2)	C13—C14	1.366 (4)
N4—C41	1.355 (2)	C14—C15	1.375 (5)
N4—C4	1.398 (2)	C15—C16	1.383 (4)
O41—C41	1.221 (2)	C31—C32	1.500 (3)
C2—C3	1.371 (2)	C41—C42	1.507 (2)
O2—S1—O1	121.58 (13)	N4—C4—C3	124.00 (14)
O2—S1—N1	104.84 (9)	C4—C5—N1	106.92 (14)
O1—S1—N1	105.31 (10)	C12—C11—C16	121.1 (2)
O2—S1—C11	110.12 (13)	C12—C11—S1	118.70 (15)
O1—S1—C11	109.29 (10)	C16—C11—S1	120.19 (18)
N1—S1—C11	104.10 (8)	C11—C12—C13	119.0 (2)
C2—N1—C5	109.99 (14)	C14—C13—C12	120.4 (2)
C2—N1—S1	124.17 (12)	C13—C14—C15	120.0 (3)
C5—N1—S1	125.82 (13)	C14—C15—C16	121.1 (2)
C41—N4—C4	124.58 (14)	C15—C16—C11	118.3 (2)
C3—C2—N1	107.68 (15)	O31—C31—C3	120.55 (15)
C2—C3—C4	107.44 (14)	O31—C31—C32	120.97 (16)
C2—C3—C31	126.07 (15)	C3—C31—C32	118.48 (15)
C4—C3—C31	126.42 (14)	O41—C41—N4	121.58 (16)
C5—C4—N4	128.05 (15)	O41—C41—C42	122.54 (16)
C5—C4—C3	107.94 (14)	N4—C41—C42	115.89 (15)
O2—S1—N1—C2	170.03 (18)	O2—S1—C11—C12	−153.89 (15)
O1—S1—N1—C2	40.67 (19)	O1—S1—C11—C12	−17.91 (17)
C11—S1—N1—C2	−74.28 (18)	N1—S1—C11—C12	94.19 (15)
O2—S1—N1—C5	−12.0 (2)	O2—S1—C11—C16	26.3 (2)
O1—S1—N1—C5	−141.39 (17)	O1—S1—C11—C16	162.31 (18)
C11—S1—N1—C5	103.66 (17)	N1—S1—C11—C16	−85.59 (18)
C5—N1—C2—C3	1.4 (2)	C16—C11—C12—C13	−1.2 (3)
S1—N1—C2—C3	179.65 (13)	S1—C11—C12—C13	179.04 (14)
N1—C2—C3—C4	−0.3 (2)	C11—C12—C13—C14	1.0 (3)
N1—C2—C3—C31	176.91 (16)	C12—C13—C14—C15	0.0 (4)
C41—N4—C4—C5	−19.9 (3)	C13—C14—C15—C16	−0.9 (4)
C41—N4—C4—C3	159.32 (17)	C14—C15—C16—C11	0.8 (4)
C2—C3—C4—C5	−0.90 (19)	C12—C11—C16—C15	0.3 (3)
C31—C3—C4—C5	−178.12 (16)	S1—C11—C16—C15	−179.91 (19)
C2—C3—C4—N4	179.77 (15)	C2—C3—C31—O31	−164.50 (18)
C31—C3—C4—N4	2.6 (3)	C4—C3—C31—O31	12.2 (3)
N4—C4—C5—N1	−178.99 (16)	C2—C3—C31—C32	15.5 (3)
C3—C4—C5—N1	1.73 (19)	C4—C3—C31—C32	−167.8 (2)
C2—N1—C5—C4	−2.0 (2)	C4—N4—C41—O41	0.3 (3)
S1—N1—C5—C4	179.82 (13)	C4—N4—C41—C42	−179.52 (16)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD* (McArdle, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *OSCAIL* (McArdle, 1995).

References

Carmona, O., Greenhouse, R., Landeros, R. & Muchowski, J. M. (1980). *J. Org. Chem.* **45**, 5336–5339.
Carson, J. R. & Davis, N. M. (1981). *J. Org. Chem.* **46**, 839–843.
Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Kakushima, M. & Frenette, R. J. (1984). *Org. Chem.* **49**, 2025–2027.

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Kakushima, M., Hamel, P., Frenette, R. & Rokach, J. (1983). *J. Org. Chem.* **48**, 3214–3219.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65–65.

Rokach, J., Hamel, P., Kakushima, M. & Smith, G. M. (1981). *Tetrahedron Lett.* **22**, 4901–4904.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen.

Stewart, J. J. P. (1985). *MOPAC*. QCPE Program 445, Version 6.0, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405, USA.

Xiao, D., Schreier, J. A., Cook, J. H., Seybold, P. G. & Ketcha, D. M. (1996). *Tetrahedron Lett.* **37**, 1523–1526.

Xu, R. X., Anderson, H. J., Gogan, N. J., Loader, C. E. & McDonald, R. (1981). *Tetrahedron Lett.* **22**, 4899–4900.

o780 David A Grossie *et al.* • $C_{14}H_{14}N_2O_4S$ *Acta Cryst.* (2001). E**57**, o778–o780