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1-Methyl-3-(4-methylphenylsulfonyl)-2-(4-methylphenylsulfonylimino)benzimidazole

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.127
Data-to-parameter ratio = 16.4

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

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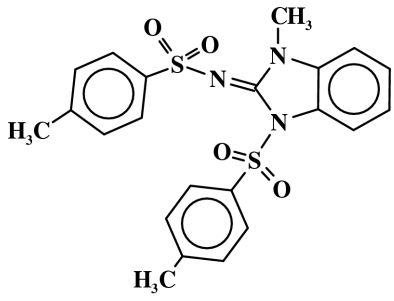
The title compound, $C_{22}H_{21}N_3O_4S_2$, is the product of the nucleophilic attack on a tosyl chloride by 2-amino-1-methylbenzimidazole. The compound contains two tosyl groups, one directly attached to an imidazole ring nitrogen and the other to the exocyclic N atom. The exocyclic N atom is bonded to the imidazole ring through a double bond [1.297 (3) Å]. The compound was also characterized by ^{1}H NMR spectroscopy.

Comment

Our research group is interested in the synthesis and characterization of metal complexes of sulfonamides (Cabaleiro *et al.*, 2000). These ligands are easily obtained by direct reaction of the corresponding amine and tosyl chloride. However, in the course of the reaction between tosyl chloride and 2-amino-1-methylbenzimidazole, the title compound, (I), was obtained as the result of a double-tosylation on the amine group and on a nitrogen of the imidazole ring.



(I)

2-Amino-1-methylbenzimidazole is usually considered to be an aromatic bicycle with an exocyclic amine group. However, the substitution of an amine hydrogen by an electron-withdrawing group causes lack of aromaticity and a tautomeric displacement towards the imine form. Under these conditions, substitution will be on the H atom of the imidazole ring nitrogen. The exocyclic nitrogen is bonded to the imidazole ring through a double bond, with a length of 1.297 (3) Å. This distance is shorter than those found in other compounds with this skeleton, either organic (Benvenuti *et al.*, 1995), or coordination compounds (Garnovskii *et al.*, 1996). The imidazole ring is not aromatic, but its planarity is maintained due to the sp^2 character of all five atoms (r.m.s. deviation = 0.0151 Å). The exocyclic S2 and N1 atoms deviate from the best plane of the imidazole ring by 0.210 (1) and 0.086 (2) Å, respectively.

The two tosyl groups present in the compound are not equivalent, and the main difference lies in the sulfur environment. Focusing on the S—N bond, one displays a bond distance of 1.6900 (19) Å, but the other one presents a value of

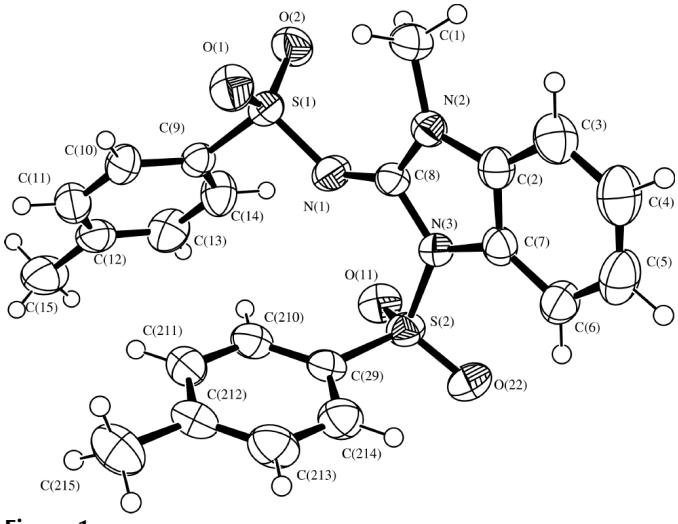


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level (Farrugia, 1998).

1.5896 (18) Å. The value expected for this kind of bond is around 1.64 Å (Allen *et al.*, 1987). The shorter one corresponds to the tosyl group bonded to the exocyclic N and the conjugation probably plays an important role in the shortening of this bond. Indeed, assuming a value for a single N—S bond of 1.71 Å (Allen *et al.*, 1987), the bond order could be calculated as 1.58 using the Pauling (1947) method ($d_n - d = -0.60\log n$, where d_n is the bond length for bond order n, and d is the length of the single bond).

Although the H atoms have been included in their idealized positions, some of them are situated close to the sulfonyl O atoms, providing evidence for C—H···O hydrogen bonds (Taylor & Kennard, 1982) (Table 2). Similarly, some interactions between C—H groups and the π clouds of the rings are present in the compound. In Table 2, these interactions are set out. The intramolecular interactions might be due to geometrical constraints, but intermolecular ones may be assumed to play a significant role in the packing arrangement.

Experimental

The title compound was prepared by reaction of 2-amino-1-methylbenzimidazole (0.5 g, 3.4 mmol) and 4-methylphenylsulfonyl chloride (1.3 g, 6.8 mmol) in a 1:2 ratio in dichloromethane. A dilute aqueous solution of K_2CO_3 was added to the mixture until pH 10 was attained and the resultant white product collected by filtration of the organic phase and dried *in vacuo*. The product was recrystallized from $CH_3CN/(CH_3)_2CO$ (1:1) to give crystals suitable for X-ray diffraction studies. The solid was identified by elemental analysis as the title compound. Found: C 57.5, H 4.9, N 9.3, S 14.0%; calculated for $C_{22}H_{21}N_3O_4S_2$: C 58.0, H 4.6, N 9.2, S 14.1%. The ^{1}H NMR spectrum of the compound was recorded on a Bruker ARX-400 MHz spectrometer in $CDCl_3$ solution with TMS as an internal reference. The spectrum shows three peaks as singlets at δ 2.35, 2.50 and 3.93 p.p.m. corresponding to the three methyl groups, whose C atoms were labelled as C15, C215 and C1, respectively. The signals corresponding to the aromatic rings appear between δ 6.95 and 8.25 p.p.m.

Crystal data

$C_{22}H_{21}N_3O_4S_2$	$Z = 2$
$M_r = 455.54$	$D_x = 1.425$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 7.9692$ (8) Å	Cell parameters from 57 reflections
$b = 11.1288$ (11) Å	$\theta = 3$–27°
$c = 13.5622$ (13) Å	$\mu = 0.29$ mm^{-1}
$\alpha = 107.529$ (2)°	$T = 293$ (2) K
$\beta = 104.567$ (2)°	Block, colourless
$\gamma = 101.135$ (2)°	0.53 × 0.28 × 0.16 mm
$V = 1061.92$ (18) Å^3	

Data collection

CCD area detector diffractometer	3401 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.031$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.0°$
$T_{min} = 0.777$, $T_{max} = 0.956$	$h = -10 \rightarrow 9$
6648 measured reflections	$k = -14 \rightarrow 13$
4641 independent reflections	$l = 0 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{max} = 0.004$
$S = 1.00$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
4641 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}
283 parameters	

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4319 (16)	N1—C8	1.297 (3)
S1—O2	1.4342 (16)	N2—C8	1.351 (3)
S1—N1	1.5896 (18)	N2—C2	1.399 (3)
S1—C9	1.759 (2)	N2—C1	1.458 (3)
S2—O11	1.4148 (16)	N3—C8	1.404 (3)
S2—O22	1.4238 (17)	N3—C7	1.416 (3)
S2—N3	1.6900 (19)	C2—C7	1.385 (3)
S2—C29	1.747 (2)		
N1—S1—C9	99.34 (10)	C7—C2—N2	108.1 (2)
N3—S2—C29	103.17 (10)	C2—C7—N3	106.10 (18)
C8—N1—S1	129.56 (17)	N1—C8—N2	133.5 (2)
C8—N2—C2	110.05 (18)	N1—C8—N3	119.6 (2)
C8—N3—C7	108.79 (18)	N2—C8—N3	106.85 (17)
C8—N3—S2	123.26 (15)		
S2—N3—C7—C2	−170.45 (15)	C7—N3—C8—N1	−175.25 (19)
C2—N2—C8—N1	176.3 (2)	S2—N3—C8—N2	171.15 (14)

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

*Cg*1 stands for the centroid of the imidazole ring, *Cg*2 for the centroid of the benzene ring C2–C7, *Cg*3 for the centroid of the phenyl ring C9–C14 and *Cg*4 for the centroid of the phenyl ring C29–C214.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···O1	0.96	2.58	3.114 (3)	115
C6—H6···O22	0.93	2.35	2.914 (3)	119
C10—H10···O1	0.93	2.52	2.897 (3)	105
C6—H6···O22^{i}	0.93	2.59	3.417 (3)	149
C13—H13···O1^{ii}	0.93	2.46	3.361 (3)	164
C210—H210···*Cg*3	0.93	3.03	3.844 (3)	147
C11—H11···*Cg*2^{iii}	0.93	2.76	3.624 (3)	154
C215—H21*B*···*Cg*1^{iv}	0.96	3.19	3.551 (3)	104
C215—H21*B*···*Cg*4^{iv}	0.96	2.98	3.756 (3)	138

Symmetry codes: (i) $-x, -y, 2-z$; (ii) $x-1, y, z$; (iii) $x, 1+y, z$; (iv) $1-x, 1-y, 2-z$.

All H atoms in the molecule were refined using a riding model (*HFIX* 43 for aromatic and *HFIX* 137 for methyl groups).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1998); software used to prepare material for publication: *SHELXL*97.

All crystallographic calculations were performed at the site fergus.uvigo.es (http://angus.uvigo.es). This study was carried out with financial support by the Xunta de Galicia (PGIDT99PXI20306B).

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