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(3-Bromo-1-phenylsulfonyl-2-indolyl)methyl Benzoate

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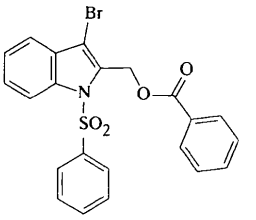
Abstract

In the title compound, $C_{22}H_{16}BrNO_4S$, the phenylsulfonyl group is nearly perpendicular [94.7 (1)°] to the indole ring system, while the other phenyl ring (of the benzoyloxymethyl substituent) is inclined at an angle of 85.9 (2)° to it. The two phenyl rings are inclined at an angle of 112.9 (3)° with respect to one another. The geometry around the S atom is distorted from the ideal tetrahedral geometry. This is evident from the deviations of the values of the bond angles around sulfur from 108.8°.

Comment

The indole ring system is present in a number of natural products, many of which are found to possess psychotropic, antidepressant and hypertensive properties (Seetharaman & Rajan, 1995). They also exhibit antimicrobial (El-sayed *et al.*, 1986), anti-inflammatory (Rodriguez *et al.*, 1985) and anti-implantation activity in rats. The study of the title compound, (I), was undertaken because very little crystallographic information is available on non-steroidal indole derivatives (Chakraborthy & Talapatra, 1986).



(I)

A *ZORTEP* (Zsolnai, 1995) plot of the molecule of (I) is shown in Fig. 1. The S—O, S—C and S—N bond distances are 1.435 (5), 1.767 (7) and 1.685 (5) Å, respectively, and are comparable with those found for another phenylsulfonyl group attached to an indole ring system (Seetharaman & Rajan, 1995). The C3—Br bond distance, 1.871 (6) Å, is in agreement with the reported value of 1.898 (2) Å (Shanmuga Sundara Raj *et al.*, 1994). The relatively large values of the C—N distances in the indole moiety [C2—N1 1.422 (8) and C9—N1 1.450 (8) Å] are due to the electron-withdrawing character of the phenylsulfonyl group. The sum of the angles about the N1 atom [354.9 (4)°] is less than the sum of the angles about the corresponding atom of a related structure [359.2 (3)°; Hökelek *et al.*, 1994]. The bond angles around the S10 atom are distorted from the ideal values for tetrahedral geometry (108.8°; Singh *et al.*, 1985); this distortion is further supported by the short non-bonded distances in this moiety, *i.e.* C13···O11 2.604 (8), C13···O12 2.634 (8) and N1···O12 2.502 (5) Å.

The indole ring system is nearly planar, as observed in many natural product derivatives (Vijayalakshmi & Srinivasan, 1975; Yamane *et al.*, 1977). The phenylsulfonyl group is perpendicular to the indole moiety. The plane through the phenyl ring of the phenylsulfonyl substituent makes an angle of 92.5 (2)° with the indole

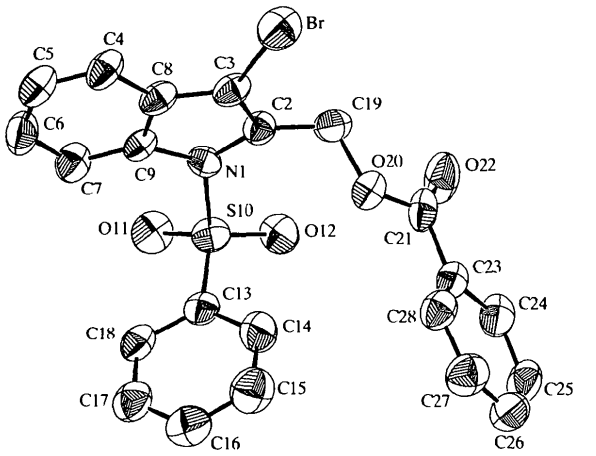


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

system. The angle between the other phenyl ring and the indole ring is 85.9 (2)°.

The packing of the molecules in the unit cell is governed by van der Waals forces. There are three short intermolecular distances present [C7···O11(x, y, z) 3.016 (1), C18···O22(x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) 3.138 (1) and C17···O22(x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) 3.180 (1) Å]. The molecular packing is stabilized by possible hydrogen-bond-like weak C—H···O interactions.

Experimental

The title compound was synthesized by a reductive condensation process (Mohanakrishnan & Srinivasan, 1993). Good quality crystals were obtained from methanol.

Crystal data

$C_{22}H_{16}BrNO_4S$
M_r = 470.33
Monoclinic
$P2_1/c$
a = 9.012 (2) Å
b = 13.492 (2) Å
c = 16.808 (2) Å
β = 95.991 (1)°
V = 2032.5 (6) Å^3
Z = 4
D_x = 1.537 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5–22°
μ = 2.154 mm^{-1}
T = 273 (2) K
Prism
0.55 × 0.40 × 0.37 mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2836 measured reflections
2638 independent reflections
1767 reflections with $I > 2\sigma(I)$

R_{int} = 0.041
θ_{max} = 22.55°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
2 standard reflections
every 200 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.131
S = 1.069
2638 reflections
263 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 5.3546P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.531 e Å^{-3}
$\Delta\rho_{min}$ = −0.521 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0017 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.422 (8)	C3—C8	1.441 (9)
N1—C9	1.450 (8)	C3—Br	1.871 (6)
N1—S10	1.685 (5)	S10—O11	1.427 (5)
C2—C3	1.344 (8)	S10—O12	1.443 (5)
C2—C19	1.501 (9)	S10—C13	1.767 (7)
C2—N1—C9	108.4 (5)	C8—C9—N1	106.1 (5)
C2—N1—S10	125.9 (4)	O11—S10—O12	120.1 (3)
C9—N1—S10	120.6 (4)	O11—S10—N1	105.8 (3)
C3—C2—N1	107.6 (6)	O12—S10—N1	106.0 (3)
C3—C2—C19	126.7 (6)	O11—S10—C13	108.8 (3)
N1—C2—C19	124.8 (5)	O12—S10—C13	109.9 (3)
C2—C3—C8	110.6 (6)	N1—S10—C13	105.2 (3)
C2—C3—Br	126.1 (6)	C14—C13—S10	119.2 (6)
C8—C3—Br	123.1 (5)	C18—C13—S10	120.4 (5)
C7—C9—N1	131.2 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O20	0.93	2.584	3.413 (9)	148.7
C18—H18···O22^i	0.93	2.515	3.138 (8)	124.6
C17—H17···O12^i	0.93	2.643	3.507 (8)	154.7

Symmetry code: (i) x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

Data collection: *P*3 (Siemens, 1994). Cell refinement: *P*3. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PT1045). Services for accessing these data are described at the back of the journal.

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Complexes Between L-Leucine and its Precipitants

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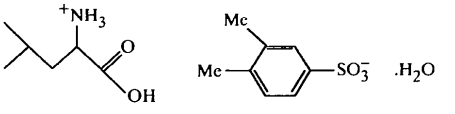
Abstract

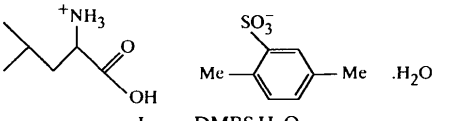
The complexes between L-leucine and aromatic sulfonic acids, L-leucine 3,4-dimethylbenzenesulfonate monohydrate ($C_6H_{14}NO_2^+.C_8H_9O_3S^-.H_2O$), L-leucine 2,5-dimethylbenzenesulfonate monohydrate ($C_6H_{14}NO_2^+.C_8H_9O_3S^-.H_2O$), L-leucine 4-methylbenzenesulfonate monohydrate ($C_6H_{14}NO_2^+.C_7H_7O_3S^-.H_2O$), as well as L-leucine benzenesulfonate monohydrate, exhibit a striking similarity in their packing schemes, which are dominated by van der Waals stacking of the hydrogen-bonded molecular double layers. The tightness of packing of double layers is most likely related to the solubility of the complexes.

Comment

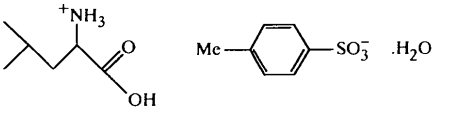
L-Leucine (Leu) is one of the essential mammalian amino acids and is used for intravenous feeding solution. Purification of Leu from hydrolysate of proteins is quite difficult because the hydrolysate contains a large amount of L-isoleucine (Ile) and L-valine (Val). These three amino acids have very similar crystal structures (Harding & Howieson, 1976; Torii & Iitaka, 1970, 1971), thus repetition of the recrystallization of Leu has been ineffective for purification because of formation of mixed crystals. Since the 1950s, many complexes between Leu and aromatic sulfonic acids (called precipitants) have been studied in order to purify Leu efficiently, and some of them are effective for the isolation of Leu. Among these precipitants, 3,4-dimethylbenzenesulfonic acid (Nagai, 1963) (*o*-DMBS) has extreme selectivity for Leu and has been used industrially. A number of precipitants resembling *o*-DMBS are known, *i.e.* 2,5-dimethylbenzenesulfonic acid (*p*-DMBS), 2,4-dimethylbenzenesulfonic acid (*m*-DMBS), *p*-toluenesulfonic acid (*p*-TS) (Hongo *et al.*, 1979) and benzenesulfonic acid (BS) (Hongo *et al.*, 1979). These precipitants form complexes with Leu, but the solubilities of the complexes are different to one another. The reduced solubilities based on Leu at 283 K are 0.82 g/100 g H_2O for the *o*-DMBS complex, 0.96 g/100 g H_2O for the *p*-DMBS complex, 6.24 g/100 g H_2O for the *m*-DMBS complex, 5.82 g/100 g H_2O for the *p*-TS complex and 7.66 g/100 g H_2O for the BS complex. The crystal structures of these five complexes were determined in order to elucidate the relationship between packing arrangement and functions as a precipitant, such as selectivity for Leu and reduced solubility. However, the results for the complex with BS have already been reported (Kimoto *et al.*, 1989) and the refinement of the complex with *m*-DMBS was unsatisfactory. Thus, we report here the crystal structures of the remaining three complexes and compare them with the results for the complex with BS.



Leu.*o*-DMBS.H_2O



Leu.*p*-DMBS.H_2O



Leu.*p*-TS.H_2O

All but one of these four complexes crystallize in the orthorhombic space group $P2_12_12_1$ with similar cell parameters. The crystal of the *m*-DMBS complex also