

4-(4-Bromophenyl)-2-methyl-1,3-thiazole

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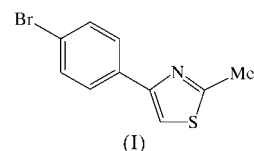
In the structure of the title compound, C₁₀H₈BrNS, the dihedral angles between the planes of the thiazole and aryl rings, *viz.* 4.2 (6) and 7.5 (6)° for the two independent molecules, are consistent with insignificant molecular perturbation by the weak intermolecular contacts. The molecules are close to being related by a non-crystallographic inversion centre, with C–H···π and π–π intermolecular interactions observed.

Comment

In earlier reports (Sánchez-Viesca & Gómez, 1998, and references therein; Sánchez-Viesca & Berros, 1999), we described the synthesis of a large series of new polysubstituted 2,4-diarylthiazoles. An interesting structural feature of these compounds is the possibility of rotameric isomerism, as a result of free rotation around the σ bond joining the thiazole and aryl moieties; this rotation is possible because of the existence of weak hydrogen bonds. Clear evidence was found that preferred rotamers are present in solution, as evidenced by ¹H NMR spectroscopy (Sánchez-Viesca & Berros, 2002), including experiments 'at infinite dilution' and correlation techniques, such as nuclear Overhauser effect spectroscopy and heteronuclear multiple-bond correlation. However, it remains difficult to predict which rotamer will be stabilized in the solid state. We suppose that potential intra- and intermolecular non-covalent interactions, mainly hydrogen bonds, are essential during the crystallization processes of these compounds. In order to determine the parameters defining these interactions, the X-ray structure determination of 2,4-diarylthiazoles with a variety of substituents is a powerful tool.

In a previous work (Bernès *et al.*, 2002), we concluded that, with the same substituents on the aryl ring, the nature of the group at the 2-position of the thiazole moiety determines

which rotamer is stabilized in the solid state, *viz.* a flat rotamer for a poor donor group at the 2-position and a twisted rotamer for a group able to form intermolecular hydrogen bonds. In the title compound, (I), the substituent is a methyl group, so a flat rotamer is expected in the solid state. The aryl moiety is a *p*-bromophenyl group, *i.e.* a fragment with local C_{2v} symmetry and *ortho* positions occupied by equivalent H atoms. Thus, there is only one possibility for the formation of an intramolecular hydrogen bond, *i.e.* that in which the thiazole N atom is considered as a potential acceptor.



The asymmetric unit of (I) contains two independent molecules (Fig. 1) with very similar geometries (Table 1). The two residues are related by a non-crystallographic inversion centre. An almost perfect fit is obtained between one molecule and the inverted second molecule, with an r.m.s. deviation of 0.037 Å. Both independent molecules are virtually planar; the r.m.s. deviation from the N1/C2/S1/C3–C10 least-squares

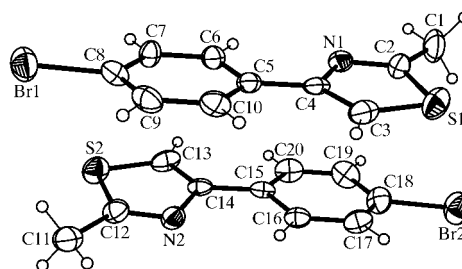


Figure 1

A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level.

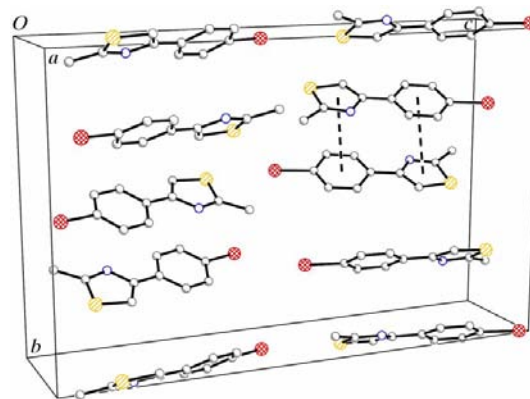


Figure 2

The packing structure of (I). One complete cell (eight molecules) is displayed. For the asymmetric unit, π–π contacts between the rings are represented by dashed lines.

plane is 0.034 (9) Å, while the corresponding deviation for the S2-containing molecule is 0.061 (10) Å. The dihedral angles between the mean planes formed by the thiazole ring and the aryl ring are 4.2 (6) and 7.5 (6)° for the S1- and S2-containing residues, respectively. The *p*-bromophenyl substituent at the 4-position exhibits no significant participation in the definition of the dihedral angle and does not participate in the intermolecular hydrogen-bonding scheme, as is seen in related thiazole derivatives (Caldwell *et al.*, 1987; Newton *et al.*, 1967). Taking into consideration the partial π character of the C4—C5 and C14—C15 bonds (Table 1), (I) can be described as the aromatic rotamer of the thiazole under study. In other words, the aromatic planar nature of the molecules has not been disturbed by intermolecular interactions (see below), at least in the solid state.

The flat conformation of (I) facilitates an interaction between the thiazole N atom and the H atom bonded to atom C6 (or C16). The observed N \cdots H separations (Table 2) can be considered as actual contacts, the distances being 0.27 (S1-containing residue) and 0.29 Å (S2-containing residue) shorter than the van der Waals distance. However, the D—H \cdots A angles are characteristic of very low electrostatic interaction energies, *i.e.* very weak intramolecular hydrogen bonds (Mascal, 1998).

The main intermolecular interaction is observed within the asymmetric unit; the non-crystallographic symmetry that relates independent residues allows π – π interactions between the five- and six-membered rings. The observed distances between the centroids of stacked rings are 3.751 (7) and 3.780 (7) Å. These pairs of molecules are stacked along the *b* axis, forming a crystal packing of segregated stacks (Fig. 2). However, these interactions are found to be significantly longer than those observed in similar crystal structures. For instance, in a thiabendazolium derivative (Prabakaran *et al.*, 2000), the shortest π – π contacts involving the thiazole ring are 3.665 and 3.669 Å. In another report on the structure of 2,4,6-triphenoxy-1,3,5-triazine, very weak π – π contacts are reported, with a separation of 3.301 Å (Thalladi *et al.*, 1998). The last kind of intermolecular interaction observed in (I) is a C—H \cdots π contact between symmetry-related molecules (Malone *et al.*, 1997), *e.g.* C20—H20A with a Br1-containing six-membered ring (symmetry code for the six-membered ring: $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$), with a C—H \cdots π separation of 2.93 Å. The weakness of the π – π and C—H \cdots π interactions observed in (I) could explain why finding a suitable single crystal for the present study was difficult (see *Experimental*).

In conclusion, we have established that, for the 2,4-substituted thiazole under consideration, a flat rotamer is stabilized in the solid state and remains unperturbed by weak intermolecular interactions. In line with our previous report (Bernès *et al.*, 2002), the substituent on the aryl moiety plays no significant role in the definition of the stabilized rotamer.

Experimental

The title compound was prepared according to the methods described by Sánchez-Viesca & Berros (1999) and Katritzky & Rees (1984).

Crystal data

C₁₀H₈BrNS
M_r = 254.14
 Orthorhombic, *P*2₁2₁2₁
a = 5.7339 (7) Å
b = 14.8229 (15) Å
c = 23.469 (2) Å
V = 1994.7 (4) Å³
Z = 8
D_x = 1.693 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 58 reflections
 θ = 4.8–11.6°
 μ = 4.28 mm^{−1}
T = 296 (2) K
 Plate, colourless
 0.40 × 0.32 × 0.04 mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (XSCANS; Siemens, 1996)
T_{min} = 0.297, *T_{max}* = 0.841
 3380 measured reflections
 2970 independent reflections
 1501 reflections with *I* > 2 σ (*I*)
R_{int} = 0.045

θ_{\max} = 25.0°
h = −6 → 4
k = −17 → 1
l = −27 → 1
 2 standard reflections every 48 reflections
 intensity decay: 8.9%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.065
wR(*F*²) = 0.166
S = 0.93
 2970 reflections
 235 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 8.6752P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983);
 1026 Friedel pairs measured
 Flack parameter = −0.05 (3)

Compound (I) crystallized as thin plates, with a tendency to systematically twin, making it difficult to select a suitable single crystal and to obtain high-quality intensity data [(*I*/ σ (*I*)) = 8.48 for

Table 1
 Selected geometric parameters (Å, °).

Br1—C8	1.880 (12)	Br2—C18	1.914 (14)
S1—C3	1.690 (14)	S2—C13	1.718 (15)
S1—C2	1.719 (13)	S2—C12	1.733 (13)
N1—C2	1.298 (14)	N2—C12	1.295 (15)
N1—C4	1.395 (15)	N2—C14	1.384 (14)
C1—C2	1.501 (18)	C11—C12	1.493 (17)
C3—C4	1.370 (16)	C13—C14	1.341 (16)
C4—C5	1.443 (16)	C14—C15	1.471 (16)
C3—S1—C2	89.7 (7)	C13—S2—C12	89.2 (6)
C2—N1—C4	111.9 (10)	C12—N2—C14	110.4 (11)
N1—C2—C1	125.0 (12)	N2—C12—C11	125.1 (12)
N1—C2—S1	114.2 (10)	N2—C12—S2	114.5 (10)
C1—C2—S1	120.8 (10)	C11—C12—S2	120.4 (11)
C4—C3—S1	111.7 (11)	C14—C13—S2	109.8 (11)
C3—C4—N1	112.5 (11)	C13—C14—N2	116.0 (12)
C3—C4—C5	128.4 (12)	C13—C14—C15	126.5 (12)
N1—C4—C5	119.1 (11)	N2—C14—C15	117.5 (11)
N1—C4—C5—C6	3.1 (17)	N2—C14—C15—C16	−6.4 (16)

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

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C6—H6A \cdots N1	0.93	2.48	2.822 (16)	102
C16—H16A \cdots N2	0.93	2.46	2.813 (17)	102

$2\theta_{\max} = 50^\circ$]. Significant intensity decay was observed during data collection (~ 60 h). The completeness of the data was reduced to 95% because: (i) 68 reflections were rejected when processing the raw data, as these reflections deviated substantially from the expected Bragg maximum [default rejection criterion in *XSCANS* (Siemens, 1996)]; (ii) in agreement with the habit of the crystal, an absorption correction was carried out using a thin-plate model, with a minimum glancing angle of 3° ; (iii) reflection 011 was omitted as it was truncated by the beam stop. H atoms were placed in idealized positions and refined as riding atoms, with fixed isotropic displacement parameters and constrained distances ($C_{\text{aromatic}}-\text{H} = 0.93 \text{ \AA}$ and $C_{\text{methyl}}-\text{H} = 0.96 \text{ \AA}$). Although the methyl H atoms on C1 and C11 were placed geometrically, it is likely that they are, in fact, disordered.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1014). Services for accessing these data are described at the back of the journal.

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