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6-Methyl-3,8-diphenyl-5*H*-pyrazolo[3,4-e]-[1,2,4]triazolo[4,3-*b*][1,3,4]thiadiazepine

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The molecule of the title compound, $C_{19}H_{14}N_6S$, is nonplanar and possesses no crystallographic symmetry. A C—H···N intermolecular hydrogen bond is observed.

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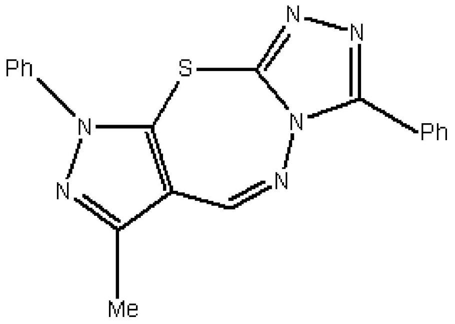
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.034
wR factor = 0.082
Data-to-parameter ratio = 12.5

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

Comment

The title compound, (I), belongs to the class of MRE (the most representative adenosine receptor antagonists) analogues, which have given one of the best results to date in terms of A_{2A} and A_3 antagonistic affinity and selectivity (Baraldi *et al.*, 1999; Baraldi & Borea, 2000), and it is thus of potential biological interest. The present structure determination of (I) was carried out in order to obtain further stereochemical information on the molecule.



(I)

In the molecule of (I) (Fig.1), the bond distances show some unexpected values (Table 1), which are not consistent with classically localized bond-valence forms. In particular, the C9═N4 and C12═N6 bonds, which are both formally double bonds, are not of equal length. In addition, the N1—N2, N3—N4 and N5—N6 bonds are expected to be shorter than the C—N single bonds, C1—N3, C2—N3 and C11—N5. In fact, none of the former three is shorter than any of the latter three. On the other hand, they are all shorter than the C12—C10 bond in the ring system. The bond distances in the C11—S1—C1 fragment are normal for their types. These two C—S bonds have effectively identical lengths, which are in the normal range.

The pyrazole and triazole rings are not coplanar, but make an angle of 50.1 (2)° with each other, while the seven-membered ring adopts a half-chair conformation, with atoms S and N4 out of the plane of the C atoms. In order to reduce steric hindrance with the central ring systems, the phenyl ring C3–C8 makes a dihedral angle of 24.8 (2)° with the triazole ring and the phenyl ring C14–C19 makes an angle of 42.4 (2)° with the pyrazole ring; they are thus not conjugated with these heterocyclic rings.

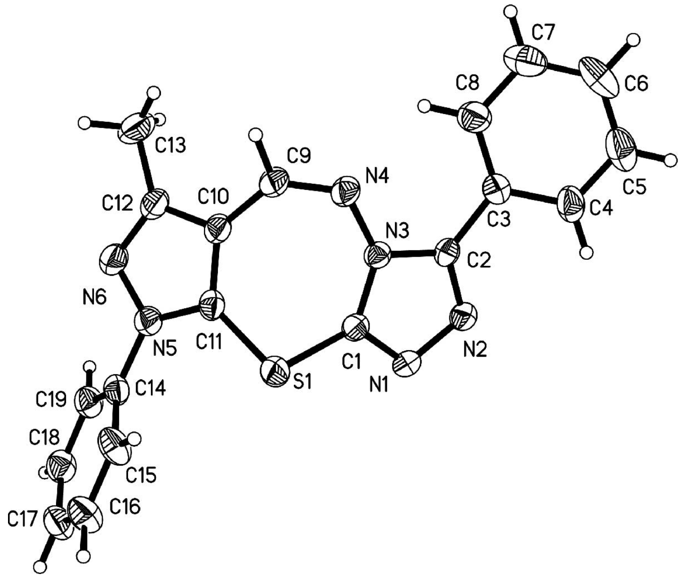


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

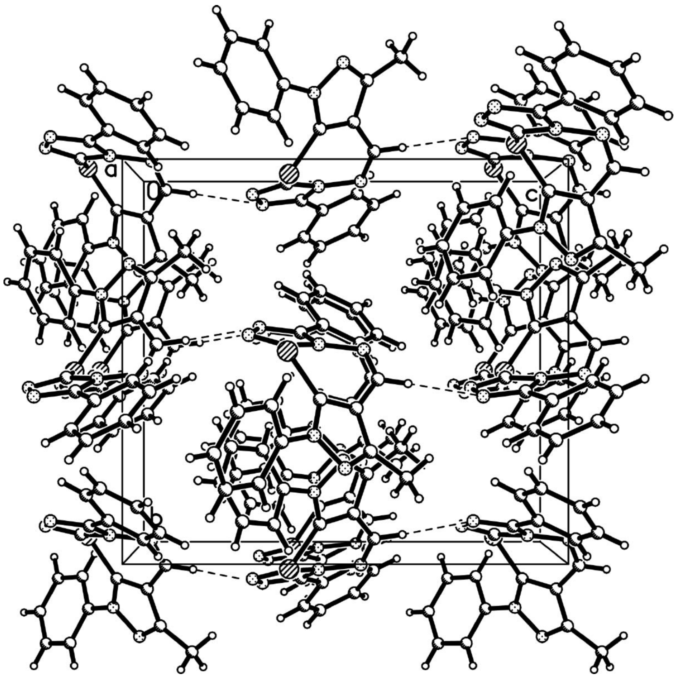


Figure 2
The molecular packing of (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

The molecules in the crystal structure of (I) are interconnected by C—H$\cdots$N hydrogen bonds (Fig. 2). Details of the intermolecular and intramolecular hydrogen-bonding interactions are given in Table 2.

Experimental

For the synthesis of (I), a solution of 5-chloro-3-methyl-1-phenylpyrazol-4-yl carboxaldehyde (0.44 g, 2 mmol) and 4-amino-5-phenyl-4-thio-1,2,4-triazole (0.39 g, 2 mmol) in ethanol was stirred under reflux for 5 h. After removal of the solvent under reduced pressure, recrystallization of the residue from ethanol gave the Schiff base. In the next step, NaH (0.024 g, 1 mmol) in dry dimethylformamide (6 ml) was placed in a 100 ml nitrogen-flushed three-necked round-bottomed flask in an ice–water bath. After 30 min, a solution of the Schiff base (0.42 g, 1 mmol) in dry dimethylformamide (10 ml) was added dropwise and the solution was stirred for 6 h under N_2 at 353 K. After completion of the reaction, the solution was poured over ice–water to give the crude product. Suitable crystals of (I) for single-crystal X-ray diffraction were obtained by evaporation of a solution in ethyl acetate.

Crystal data

$C_{19}H_{14}N_6S$
$M_r = 358.42$
Orthorhombic, $Pna2_1$
$a = 10.083$ (4) Å
$b = 12.576$ (4) Å
$c = 13.849$ (5) Å
$V = 1756.1$ (10) Å^3
$Z = 4$
$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 958 reflections
$\theta = 3.0$–22.9°
$\mu = 0.20$ mm^{-1}
$T = 295$ (2) K
Block, colourless
0.26 × 0.24 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.919$, $T_{\max} = 0.961$
9699 measured reflections
2950 independent reflections
2211 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 26.4°$
$h = -12 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.082$
$S = 1.03$
2950 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.2938P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Absolute structure: Flack (1983), with 1075 Friedel pairs
Flack parameter: 0.05 (9)

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.737 (3)	N4—C9	1.277 (3)
S1—C11	1.740 (3)	N5—N6	1.369 (3)
N1—C1	1.306 (4)	N5—C11	1.351 (3)
N1—N2	1.379 (3)	N5—C14	1.418 (3)
N2—C2	1.314 (3)	N6—C12	1.326 (4)
N3—C2	1.369 (3)	C2—C3	1.463 (4)
N3—C1	1.369 (3)	C9—C10	1.443 (4)
N3—N4	1.400 (3)	C10—C12	1.414 (4)
C1—S1—C11	97.68 (12)	N3—C1—S1	127.3 (2)
C9—N4—N3	117.5 (2)	N4—C9—C10	132.7 (3)
C11—N5—N6	111.4 (2)	C11—C10—C9	128.0 (3)
C12—N6—N5	105.5 (2)	C10—C11—S1	127.7 (2)
N2—N1—C1—S1	−172.02 (17)	C9—C10—C11—N5	173.0 (3)
C2—N3—C1—N1	−0.9 (3)	C9—C10—C11—S1	−6.6 (4)
N4—N3—C1—N1	−175.0 (2)	C11—C10—C12—C13	−176.7 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N2	0.93	2.54	2.856 (4)	100
C8—H8···N4	0.93	2.42	2.949 (4)	116
C9—H9···N2$^{\text{i}}$	0.93	2.47	3.379 (4)	166
C15—H15···S1	0.93	2.73	3.180 (3)	111

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

H atoms were positioned geometrically and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (1.5 for methyl H atoms) times U_{eq} of their carrier atoms, and C—H distances were set at 0.96 Å for the methyl H atoms and 0.93 Å for those of the other groups.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Siemens, 1995); software used to prepare material for publication: *SHELXTL-NT*.

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