

4-[(*E*)-2,6-Dichlorobenzylideneamino]-3-[1-[4-(2-methylpropyl)phenyl]ethyl]-1*H*-1,2,4-triazole-5(4*H*)-thione

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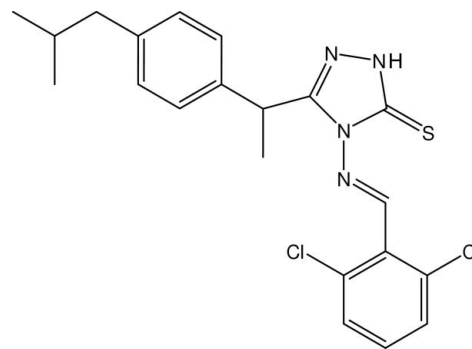
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.047; wR factor = 0.136; data-to-parameter ratio = 23.6.

In the title Schiff base compound, $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_4\text{S}$, the triazole ring makes dihedral angles of 2.15 (11) and 87.48 (11)° with the 2,6-dichlorophenyl and methylpropylphenyl rings, respectively. Weak intramolecular $\text{C}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{Cl}$ interactions generate $S(6)$ and $S(5)$ ring motifs, respectively. In the crystal structure, centrosymmetrically related molecules are linked into dimers by $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds. These dimers are arranged into sheets parallel to the ab plane and are stacked along the c axis. $\text{C}-\text{H}\cdots\pi$ interactions involving the methylpropylphenyl ring and $\pi-\pi$ interactions involving the dichlorophenyl ring [centroid-centroid distance = 3.5865 (3) Å] are also observed.

Related literature

For related literature on hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For related structures, see: Fun *et al.* (2008*a,b*). For background to the activities and applications of 1,2,4-triazole derivatives, see: Almasirad *et al.* (2004); Al-Soud *et al.* (2003); Amir & Shikha (2004); Holla *et al.* (2003); Kawashima *et al.* (1987); Palaska *et al.* (2002); Walczak *et al.* (2004); Zitouni *et al.* (2005).



Experimental

Crystal data

$\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_4\text{S}$
 $M_r = 433.40$
Triclinic, $P\bar{1}$
 $a = 8.6190$ (2) Å
 $b = 9.4441$ (2) Å
 $c = 14.4244$ (4) Å
 $\alpha = 104.669$ (2)°
 $\beta = 95.492$ (2)°

$\gamma = 110.418$ (1)°
 $V = 1042.33$ (5) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.43$ mm⁻¹
 $T = 100.0$ (1) K
 $0.29 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)
 $T_{\min} = 0.887$, $T_{\max} = 0.934$

19865 measured reflections
6032 independent reflections
4139 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.136$
 $S = 1.00$
6032 reflections

256 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2A}\cdots\text{S1}^i$	0.86	2.44	3.2849 (19)	169
$\text{C10}-\text{H10A}\cdots\text{Cl2}$	0.93	2.62	2.978 (2)	104
$\text{C10}-\text{H10A}\cdots\text{S1}$	0.93	2.52	3.2066 (19)	131
$\text{C15}-\text{H15A}\cdots\text{Cg1}^{ii}$	0.93	2.94	3.793 (3)	154

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2627).

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supplementary materials

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4-[(*E*)-2,6-Dichlorobenzylideneamino]-3-{1-[4-(2-methylpropyl)phenyl]ethyl}-1*H*-1,2,4-triazole-5(4*H*)-thione

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Comment

1,2,4-Triazoles and their derivatives represent an overwhelming and rapid developing field in modern heterocyclic chemistry. A degree of respectability has been bestowed for 1,2,4-triazole derivatives due to their antibacterial, antifungal (Zitouni *et al.*, 2005), antitubercular (Walczak *et al.*, 2004), anticancer (Holla *et al.*, 2003), antitumor (Al-Soud *et al.*, 2003), anticonvulsant (Almasirad *et al.*, 2004), antiinflammatory, and analgesic properties (Amir & Shikha, 2004). Certain 1,2,4-triazoles also find applications in the preparation of photographic plates, polymers, and as analytical agents (Kawashima *et al.*, 1987). Similarly, ibuprofen belongs to the class of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) with antipyretic, anti-inflammatory and analgesic properties (Palaska *et al.*, 2002). Our earlier studies involved synthesis of heterocyclic compounds which contain in their structures both the ibuprofen and 1,2,4-triazole fragments (Fun *et al.*, 2008*a,b*). In this connection and in continuation of our interest in the synthesis of chemically and biologically important heterocycles, we report here the crystal structure of a substituted 1,2,4-triazole Schiff base carrying only the ibuprofen moiety.

In the title Schiff base compound (Fig. 1), the 1,2,4 triazole ring (C8-C9/N1-N3) is planar with a maximum deviation of 0.009 (2) Å for atom N3. The 1,2,4 triazole ring is co-planar with the 2,6-dichlorophenyl (C11-C16) ring [dihedral angle = 2.15 (11)°] but is almost perpendicular to the methylpropylphenyl (C1-C6) ring with a dihedral angle of 87.48 (11)°. The methylidene amino linkage (N4/C10) is slightly twisted from the mean plane of the 1,2,4 triazole ring as indicated by the torsion angle C9-N3-N4-C10 of 26.4 (3)°. Weak C—H···S and C—H···Cl intramolecular interactions generate S(6) and S(5) ring motifs, respectively (Bernstein *et al.*, 1995). The bond distances and angles have normal values (Allen *et al.*, 1987) and are comparable with closely related structures (Fun *et al.*, 2008*a,b*).

In the crystal structure, centrosymmetrically related molecules are linked into dimers (Fig. 2) by N—H···S hydrogen bonds (Table 1). These dimers are arranged into sheets parallel to the *ab* plane and these sheets are stacked along the *c* axis (Fig. 3). In addition, the crystal structure is stabilized by C—H··· π interactions (Table 1) involving the C1-C6 ring (centroid Cg1) and π - π interaction involving the C11-C16 ring (centroid Cg2) [$Cg_2 \cdots Cg_2^{ii}$ = 3.5865 (3) Å, symmetry code: (ii) 1 - *x*, -*y*, -*z*].

Experimental

The title compound was obtained by refluxing 4-amino-5-[1-(4-isobutylphenyl)ethyl]-4*H*-1,2,4-triazole-3-thiol (0.01 mol) and 2,6-dichlorobenzaldehyde (0.01 mol) in ethanol (50 ml) with the addition of 3 drops of concentrated sulfuric acid for 3 h. The solid product obtained was collected by filtration, washed with ethanol and dried. Colourless single crystals suitable for X-ray analysis were obtained from a acetone-*N,N*-dimethylformamide (DMF) (1:3 *v/v*) solution by slow evaporation (yield 53%; m.p. 438–440 K)

Refinement

All H atoms were placed in calculated positions (N-H = 0.86 Å and C-H = 0.93-0.98 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. A rotating group model was used for the methyl groups.

Figures

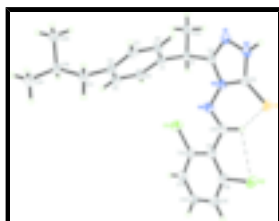


Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Weak C—H \cdots S and C—H \cdots Cl hydrogen bonds are shown as dashed lines.

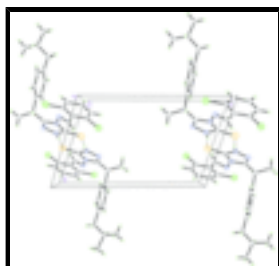


Fig. 2. Part of the crystal packing of the title compound, viewed along the *a* axis, showing hydrogen-bonded (dashed lines) dimers.

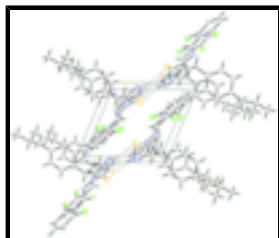


Fig. 3. The packing diagram of the title compound, viewed along the *c* axis, showing stacking of the molecular sheets. Hydrogen bonds are shown as dashed lines.

4-[(*E*)-2,6-Dichlorobenzylideneamino]-3-[1-[4-(2-methylpropyl)phenyl]ethyl]-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

$\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_4\text{S}$

$M_r = 433.40$

Triclinic, *PT*

Hall symbol: -P 1

$a = 8.6190(2) \text{ \AA}$

$b = 9.4441(2) \text{ \AA}$

$c = 14.4244(4) \text{ \AA}$

$\alpha = 104.669(2)^\circ$

$\beta = 95.492(2)^\circ$

$\gamma = 110.418(1)^\circ$

$V = 1042.33(5) \text{ \AA}^3$

$Z = 2$

$F_{000} = 452$

$D_x = 1.381 \text{ Mg m}^{-3}$

Melting point = 438–440 K

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6032 reflections

$\theta = 1.5\text{--}30.0^\circ$

$\mu = 0.43 \text{ mm}^{-1}$

$T = 100.0(1) \text{ K}$

Block, colourless

$0.29 \times 0.20 \times 0.16 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	6032 independent reflections
Radiation source: fine-focus sealed tube	4139 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.050$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{\text{max}} = 30.0^\circ$
$T = 100.0(1)$ K	$\theta_{\text{min}} = 1.5^\circ$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -13 \rightarrow 13$
$T_{\text{min}} = 0.887$, $T_{\text{max}} = 0.935$	$l = -20 \rightarrow 19$
19865 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.136$	$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
6032 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
256 parameters	$\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.79027 (6)	-0.43005 (6)	-0.06227 (3)	0.02335 (13)
Cl1	0.43164 (7)	-0.07928 (7)	0.21127 (4)	0.03523 (15)
Cl2	0.41695 (7)	-0.33808 (6)	-0.17537 (4)	0.03136 (14)

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N1	0.9611 (2)	-0.3270 (2)	0.21761 (12)	0.0244 (4)
N2	0.9465 (2)	-0.3961 (2)	0.11923 (12)	0.0240 (4)
H2A	1.0037	-0.4511	0.0971	0.029*
N3	0.7738 (2)	-0.28053 (18)	0.12730 (11)	0.0192 (3)
N4	0.6602 (2)	-0.20834 (19)	0.11584 (12)	0.0229 (4)
C1	0.9409 (2)	0.0211 (2)	0.32320 (13)	0.0218 (4)
C2	1.1052 (3)	0.0657 (2)	0.30759 (15)	0.0259 (4)
H2B	1.1515	-0.0105	0.2915	0.031*
C3	1.2013 (3)	0.2223 (2)	0.31568 (15)	0.0266 (4)
H3A	1.3109	0.2492	0.3046	0.032*
C4	1.1366 (3)	0.3403 (2)	0.34015 (14)	0.0244 (4)
C5	0.9747 (3)	0.2957 (2)	0.35952 (14)	0.0262 (4)
H5A	0.9301	0.3726	0.3786	0.031*
C6	0.8779 (3)	0.1389 (2)	0.35107 (14)	0.0234 (4)
H6A	0.7696	0.1125	0.3642	0.028*
C7	0.8319 (3)	-0.1523 (2)	0.31079 (14)	0.0225 (4)
H7A	0.7131	-0.1651	0.3013	0.027*
C8	0.8563 (2)	-0.2560 (2)	0.22068 (14)	0.0217 (4)
C9	0.8351 (2)	-0.3702 (2)	0.06064 (14)	0.0206 (4)
C10	0.5498 (2)	-0.2695 (2)	0.03633 (14)	0.0223 (4)
H10A	0.5495	-0.3578	-0.0105	0.027*
C11	0.4228 (2)	-0.2036 (2)	0.01691 (14)	0.0215 (4)
C12	0.3619 (3)	-0.1177 (2)	0.08757 (15)	0.0239 (4)
C13	0.2388 (3)	-0.0628 (2)	0.06263 (16)	0.0270 (4)
H13A	0.2011	-0.0054	0.1112	0.032*
C14	0.1729 (3)	-0.0938 (2)	-0.03479 (16)	0.0278 (5)
H14A	0.0906	-0.0570	-0.0516	0.033*
C15	0.2278 (3)	-0.1792 (3)	-0.10761 (16)	0.0284 (5)
H15A	0.1829	-0.2003	-0.1732	0.034*
C16	0.3504 (3)	-0.2325 (2)	-0.08126 (14)	0.0246 (4)
C17	1.2359 (3)	0.5077 (2)	0.34117 (15)	0.0281 (5)
H17A	1.1787	0.5286	0.2881	0.034*
H17B	1.3462	0.5147	0.3281	0.034*
C18	1.2612 (3)	0.6380 (2)	0.43631 (15)	0.0248 (4)
H18A	1.1498	0.6274	0.4512	0.030*
C19	1.3448 (3)	0.8002 (2)	0.42311 (17)	0.0331 (5)
H19A	1.3584	0.8813	0.4826	0.050*
H19B	1.2752	0.8098	0.3709	0.050*
H19C	1.4535	0.8121	0.4075	0.050*
C20	1.3655 (3)	0.6216 (3)	0.52176 (15)	0.0307 (5)
H20A	1.3751	0.7017	0.5808	0.046*
H20B	1.4763	0.6345	0.5092	0.046*
H20C	1.3109	0.5185	0.5289	0.046*
C21	0.8713 (3)	-0.2028 (3)	0.39995 (15)	0.0315 (5)
H21A	0.8010	-0.3124	0.3882	0.047*
H21B	0.8496	-0.1387	0.4564	0.047*
H21C	0.9880	-0.1890	0.4113	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0258 (3)	0.0241 (2)	0.0194 (2)	0.0112 (2)	0.00672 (19)	0.00244 (18)
C11	0.0389 (3)	0.0551 (4)	0.0221 (3)	0.0310 (3)	0.0104 (2)	0.0093 (2)
C12	0.0362 (3)	0.0338 (3)	0.0213 (3)	0.0135 (2)	0.0063 (2)	0.0036 (2)
N1	0.0296 (9)	0.0241 (8)	0.0190 (8)	0.0132 (7)	0.0055 (7)	0.0016 (7)
N2	0.0272 (9)	0.0240 (8)	0.0228 (8)	0.0152 (7)	0.0061 (7)	0.0030 (7)
N3	0.0210 (8)	0.0184 (7)	0.0182 (8)	0.0081 (6)	0.0061 (6)	0.0043 (6)
N4	0.0241 (8)	0.0230 (8)	0.0247 (9)	0.0120 (7)	0.0080 (7)	0.0072 (7)
C1	0.0245 (10)	0.0248 (10)	0.0144 (9)	0.0095 (8)	0.0034 (7)	0.0036 (7)
C2	0.0280 (10)	0.0235 (10)	0.0270 (11)	0.0134 (8)	0.0080 (8)	0.0033 (8)
C3	0.0245 (10)	0.0280 (10)	0.0245 (10)	0.0090 (8)	0.0086 (8)	0.0037 (8)
C4	0.0299 (10)	0.0252 (10)	0.0159 (9)	0.0108 (8)	0.0050 (8)	0.0023 (8)
C5	0.0293 (10)	0.0250 (10)	0.0242 (10)	0.0140 (8)	0.0062 (8)	0.0020 (8)
C6	0.0245 (10)	0.0261 (10)	0.0205 (9)	0.0124 (8)	0.0072 (8)	0.0037 (8)
C7	0.0251 (10)	0.0229 (9)	0.0195 (9)	0.0103 (8)	0.0064 (8)	0.0042 (7)
C8	0.0249 (10)	0.0194 (9)	0.0199 (9)	0.0075 (8)	0.0069 (7)	0.0051 (7)
C9	0.0227 (9)	0.0165 (8)	0.0212 (9)	0.0067 (7)	0.0071 (7)	0.0039 (7)
C10	0.0216 (9)	0.0203 (9)	0.0237 (10)	0.0066 (8)	0.0081 (8)	0.0054 (7)
C11	0.0192 (9)	0.0203 (9)	0.0235 (10)	0.0049 (7)	0.0062 (8)	0.0072 (7)
C12	0.0228 (10)	0.0270 (10)	0.0223 (10)	0.0093 (8)	0.0068 (8)	0.0082 (8)
C13	0.0225 (10)	0.0300 (11)	0.0323 (11)	0.0125 (8)	0.0106 (8)	0.0113 (9)
C14	0.0219 (10)	0.0300 (11)	0.0356 (12)	0.0107 (9)	0.0062 (9)	0.0158 (9)
C15	0.0274 (10)	0.0296 (11)	0.0255 (11)	0.0074 (9)	0.0028 (8)	0.0103 (8)
C16	0.0246 (10)	0.0244 (10)	0.0226 (10)	0.0065 (8)	0.0079 (8)	0.0064 (8)
C17	0.0349 (12)	0.0259 (10)	0.0224 (10)	0.0104 (9)	0.0104 (9)	0.0060 (8)
C18	0.0267 (10)	0.0220 (10)	0.0241 (10)	0.0086 (8)	0.0062 (8)	0.0053 (8)
C19	0.0390 (13)	0.0245 (10)	0.0335 (12)	0.0102 (10)	0.0105 (10)	0.0070 (9)
C20	0.0353 (12)	0.0306 (11)	0.0264 (11)	0.0164 (9)	0.0049 (9)	0.0046 (9)
C21	0.0416 (13)	0.0319 (11)	0.0234 (11)	0.0159 (10)	0.0103 (9)	0.0088 (9)

Geometric parameters (\AA , $^\circ$)

S1—C9	1.6797 (19)	C10—C11	1.472 (3)
C11—C12	1.730 (2)	C10—H10A	0.93
C12—C16	1.740 (2)	C11—C12	1.398 (3)
N1—C8	1.297 (2)	C11—C16	1.409 (3)
N1—N2	1.377 (2)	C12—C13	1.389 (3)
N2—C9	1.345 (2)	C13—C14	1.381 (3)
N2—H2A	0.86	C13—H13A	0.93
N3—C8	1.384 (2)	C14—C15	1.382 (3)
N3—C9	1.385 (2)	C14—H14A	0.93
N3—N4	1.394 (2)	C15—C16	1.381 (3)
N4—C10	1.275 (2)	C15—H15A	0.93
C1—C2	1.388 (3)	C17—C18	1.531 (3)
C1—C6	1.390 (3)	C17—H17A	0.97
C1—C7	1.530 (3)	C17—H17B	0.97

supplementary materials

C2—C3	1.388 (3)	C18—C19	1.519 (3)
C2—H2B	0.93	C18—C20	1.527 (3)
C3—C4	1.396 (3)	C18—H18A	0.98
C3—H3A	0.93	C19—H19A	0.96
C4—C5	1.388 (3)	C19—H19B	0.96
C4—C17	1.508 (3)	C19—H19C	0.96
C5—C6	1.389 (3)	C20—H20A	0.96
C5—H5A	0.93	C20—H20B	0.96
C6—H6A	0.93	C20—H20C	0.96
C7—C8	1.498 (3)	C21—H21A	0.96
C7—C21	1.529 (3)	C21—H21B	0.96
C7—H7A	0.98	C21—H21C	0.96
C8—N1—N2	104.17 (15)	C13—C12—C11	116.33 (16)
C9—N2—N1	114.24 (15)	C11—C12—C11	121.52 (16)
C9—N2—H2A	122.9	C14—C13—C12	119.57 (19)
N1—N2—H2A	122.9	C14—C13—H13A	120.2
C8—N3—C9	108.43 (15)	C12—C13—H13A	120.2
C8—N3—N4	119.01 (15)	C13—C14—C15	120.7 (2)
C9—N3—N4	132.41 (16)	C13—C14—H14A	119.6
C10—N4—N3	117.04 (16)	C15—C14—H14A	119.6
C2—C1—C6	117.99 (19)	C16—C15—C14	118.81 (19)
C2—C1—C7	121.30 (17)	C16—C15—H15A	120.6
C6—C1—C7	120.71 (18)	C14—C15—H15A	120.6
C1—C2—C3	121.00 (18)	C15—C16—C11	122.96 (19)
C1—C2—H2B	119.5	C15—C16—C12	117.26 (16)
C3—C2—H2B	119.5	C11—C16—C12	119.79 (16)
C2—C3—C4	121.3 (2)	C4—C17—C18	115.60 (17)
C2—C3—H3A	119.4	C4—C17—H17A	108.4
C4—C3—H3A	119.4	C18—C17—H17A	108.4
C5—C4—C3	117.32 (19)	C4—C17—H17B	108.4
C5—C4—C17	121.41 (18)	C18—C17—H17B	108.4
C3—C4—C17	121.22 (19)	H17A—C17—H17B	107.4
C4—C5—C6	121.51 (18)	C19—C18—C20	110.68 (17)
C4—C5—H5A	119.2	C19—C18—C17	109.89 (18)
C6—C5—H5A	119.2	C20—C18—C17	111.28 (17)
C5—C6—C1	120.83 (19)	C19—C18—H18A	108.3
C5—C6—H6A	119.6	C20—C18—H18A	108.3
C1—C6—H6A	119.6	C17—C18—H18A	108.3
C8—C7—C21	110.54 (16)	C18—C19—H19A	109.5
C8—C7—C1	108.88 (16)	C18—C19—H19B	109.5
C21—C7—C1	112.70 (16)	H19A—C19—H19B	109.5
C8—C7—H7A	108.2	C18—C19—H19C	109.5
C21—C7—H7A	108.2	H19A—C19—H19C	109.5
C1—C7—H7A	108.2	H19B—C19—H19C	109.5
N1—C8—N3	110.81 (16)	C18—C20—H20A	109.5
N1—C8—C7	126.05 (18)	C18—C20—H20B	109.5
N3—C8—C7	123.04 (17)	H20A—C20—H20B	109.5
N2—C9—N3	102.32 (15)	C18—C20—H20C	109.5
N2—C9—S1	127.33 (15)	H20A—C20—H20C	109.5

N3—C9—S1	130.33 (15)	H20B—C20—H20C	109.5
N4—C10—C11	121.60 (18)	C7—C21—H21A	109.5
N4—C10—H10A	119.2	C7—C21—H21B	109.5
C11—C10—H10A	119.2	H21A—C21—H21B	109.5
C12—C11—C16	115.84 (18)	C7—C21—H21C	109.5
C12—C11—C10	125.92 (18)	H21A—C21—H21C	109.5
C16—C11—C10	118.21 (17)	H21B—C21—H21C	109.5
C13—C12—C11	122.11 (19)		
C8—N1—N2—C9	0.0 (2)	N1—N2—C9—N3	-1.0 (2)
C8—N3—N4—C10	-158.60 (18)	N1—N2—C9—S1	177.52 (14)
C9—N3—N4—C10	26.4 (3)	C8—N3—C9—N2	1.52 (19)
C6—C1—C2—C3	-2.6 (3)	N4—N3—C9—N2	176.87 (18)
C7—C1—C2—C3	177.75 (18)	C8—N3—C9—S1	-176.89 (16)
C1—C2—C3—C4	0.3 (3)	N4—N3—C9—S1	-1.5 (3)
C2—C3—C4—C5	2.3 (3)	N3—N4—C10—C11	179.51 (17)
C2—C3—C4—C17	-175.13 (19)	N4—C10—C11—C12	-26.3 (3)
C3—C4—C5—C6	-2.6 (3)	N4—C10—C11—C16	155.8 (2)
C17—C4—C5—C6	174.83 (19)	C16—C11—C12—C13	-0.6 (3)
C4—C5—C6—C1	0.3 (3)	C10—C11—C12—C13	-178.53 (19)
C2—C1—C6—C5	2.3 (3)	C16—C11—C12—C11	177.38 (15)
C7—C1—C6—C5	-178.04 (18)	C10—C11—C12—C11	-0.6 (3)
C2—C1—C7—C8	-42.3 (2)	C11—C12—C13—C14	0.3 (3)
C6—C1—C7—C8	138.03 (19)	C11—C12—C13—C14	-177.75 (16)
C2—C1—C7—C21	80.7 (2)	C12—C13—C14—C15	0.1 (3)
C6—C1—C7—C21	-98.9 (2)	C13—C14—C15—C16	-0.2 (3)
N2—N1—C8—N3	1.0 (2)	C14—C15—C16—C11	-0.1 (3)
N2—N1—C8—C7	-175.37 (18)	C14—C15—C16—C12	-179.50 (16)
C9—N3—C8—N1	-1.7 (2)	C12—C11—C16—C15	0.5 (3)
N4—N3—C8—N1	-177.76 (17)	C10—C11—C16—C15	178.60 (19)
C9—N3—C8—C7	174.84 (17)	C12—C11—C16—C12	179.88 (15)
N4—N3—C8—C7	-1.2 (3)	C10—C11—C16—C12	-2.0 (2)
C21—C7—C8—N1	-29.1 (3)	C5—C4—C17—C18	56.3 (3)
C1—C7—C8—N1	95.2 (2)	C3—C4—C17—C18	-126.4 (2)
C21—C7—C8—N3	154.92 (18)	C4—C17—C18—C19	-173.51 (18)
C1—C7—C8—N3	-80.8 (2)	C4—C17—C18—C20	63.5 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots S1 ⁱ	0.86	2.44	3.2849 (19)	169
C10—H10A \cdots C12	0.93	2.62	2.978 (2)	104
C10—H10A \cdots S1	0.93	2.52	3.2066 (19)	131
C15—H15A \cdots Cg1 ⁱⁱ	0.93	2.94	3.793 (3)	154

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

Fig. 1

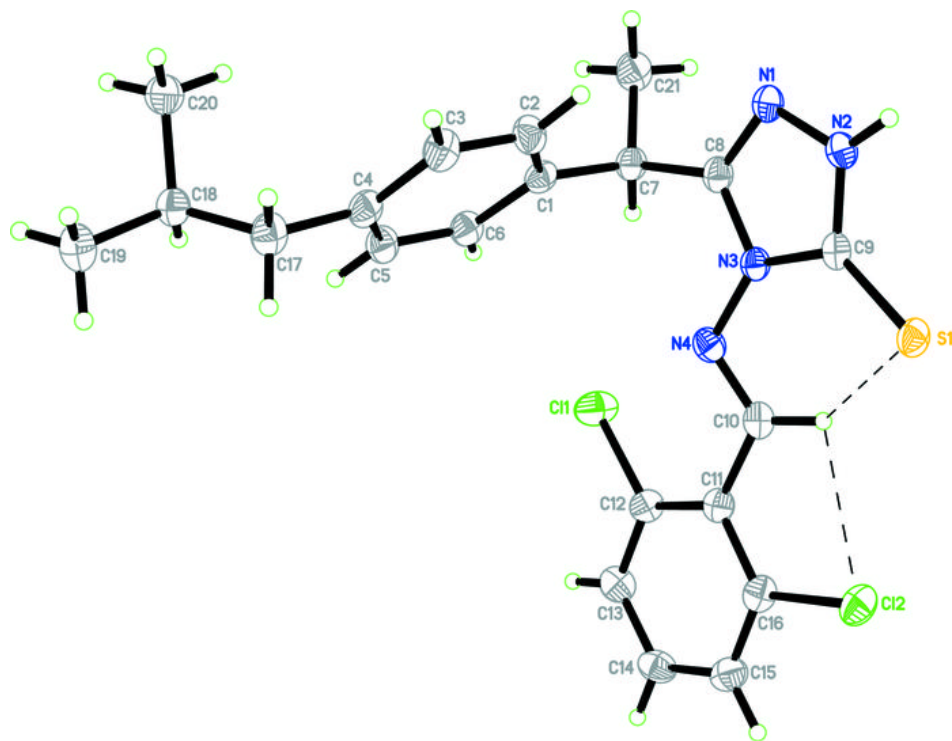


Fig. 2

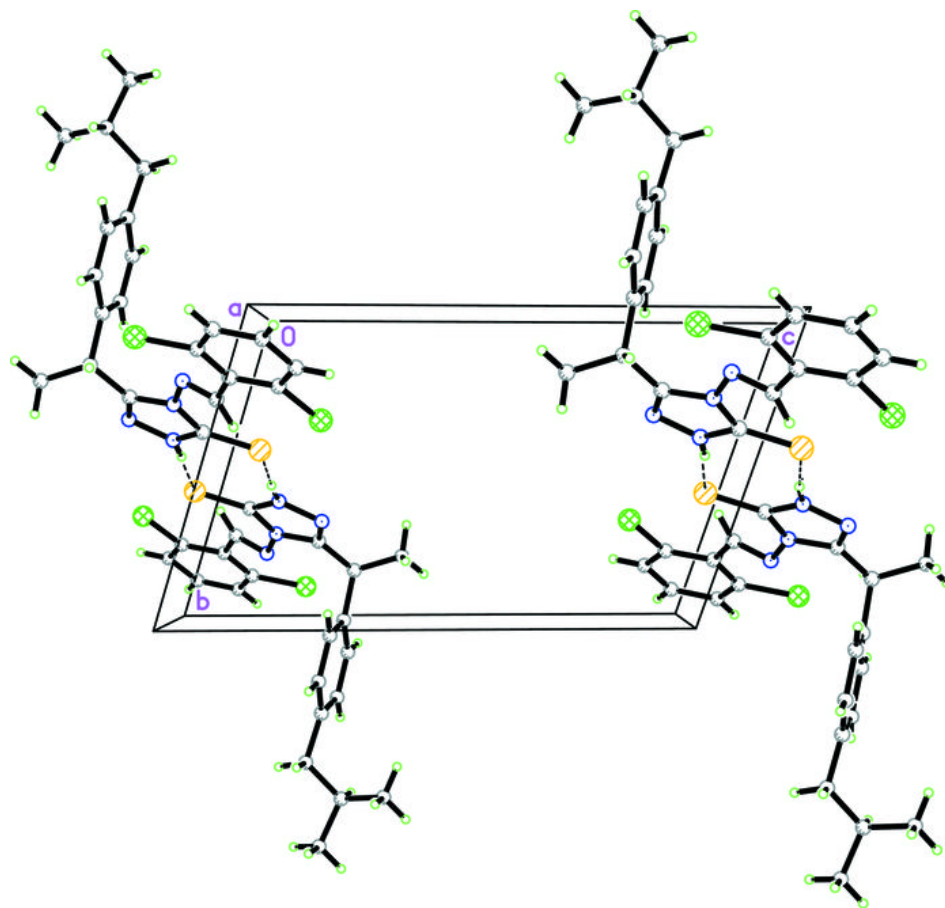


Fig. 3

