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1-(3-Chlorophenyl)-5-(4-chlorophenyl)-3-(5-chlorothiophen-2-yl)-4,5-dihydro-1*H*-pyrazole

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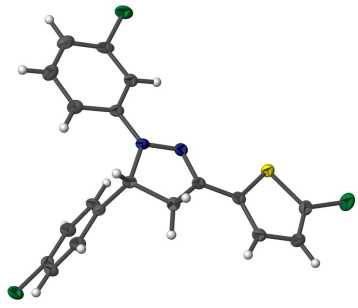
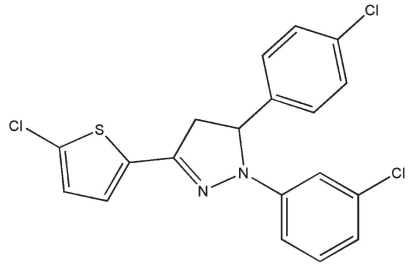
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{19}H_{13}Cl_3N_2S$, the central dihydropyrazole ring adopts an envelope conformation with the chiral C atom as the flap. In the crystal, molecules are linked by weak C—H···Cl hydrogen bonds into supramolecular chains propagating along the *b*-axis direction.

3D view



Chemical scheme



Structure description

Five-membered nitrogen heterocycles such as pyrazoles have been studied extensively for their enormous number of synthetic utilities and pharmaceutical applications. These classes of compounds have known to exhibit varied biological activities such as anti-amoebic (Abid & Azam, 2006). In view of their potential applications and in a continuation of our work on pyrazolines (Assem *et al.*, 2016), we report herein on the synthesis and crystal structure of the title compound.

The structure of the molecule is shown in Fig. 1. The central pyrazole ring adopts an envelope conformation with the C3 flap atom having a maximum deviation of 0.138 (4) Å, and puckering parameters $Q = 0.220$ (3) Å and $\varphi = 78.7$ (8)°. The mean plane through the pyrazole ring forms dihedral angles of 5.41 (17), 5.54 (16) and 76.89 (17)° with the chlorothiophene, chlorophenyl (C8–C13) and chlorophenyl (C14–C19) rings, respectively, whereas the dihedral angle between the chlorophenyl rings is 81.19 (16)°.

The title compound is chiral. In the arbitrarily chosen asymmetric molecule, the compound possess a chiral center at C3 with an *R* conformation. Since the compound crystallizes in a centrosymmetric space group, we can surmise that the compound is a racemic mixture. In the crystal, the molecules are connected by C3—H3···Cl2 interactions (Table 1) into the supramolecular chains propagating along the *b* axis.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···Cl2^{i}	0.98	2.82	3.700 (4)	150

Symmetry code: (i) $x, y+1, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{13}Cl_3N_2S$
M_r	407.73
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	7.6071 (2), 11.3292 (4), 11.7601 (4)
α, β, γ (°)	64.529 (1), 75.255 (2), 81.149 (2)
V (Å^3)	883.73 (5)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	5.83
Crystal size (mm)	0.27 × 0.24 × 0.22
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.302, 0.360
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9181, 2912, 2661
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.586
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.152, 1.06
No. of reflections	2912
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, −0.37

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

Synthesis and crystallization

To a solution of (*E*)-3-(4-chlorophenyl)-1-(5-chlorothiophen-2-yl)prop-2-en-1-one, (5 mmol) and (3-chlorophenyl)hydrazine hydrochloride (5 mmol) in methyl alcohol (25 ml), 4–5 drops of conc. hydrochloric acid were added. The mixture was refluxed on a water bath for 4 h. The progress of the reaction was monitored by TLC. After completion, the mixture was poured into ice-cold water and stirred. The solid that separated was filtered and washed with ice-cold water. The product was crystallized from methyl alcohol to get the title compound in 82% yield, m.p. 375–373 K.

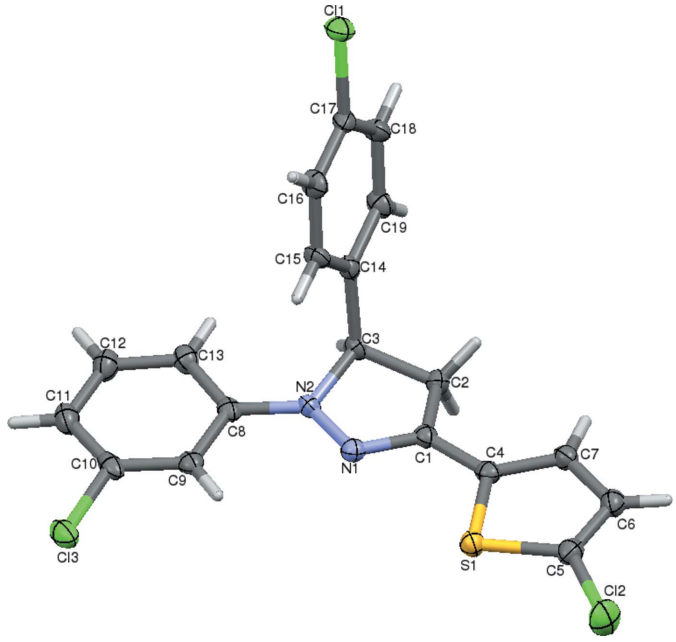


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x162048 [https://doi.org/10.1107/S2414314616020484]

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Crystal data

$C_{19}H_{13}Cl_3N_2S$
M_r = 407.73
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.6071 (2) Å
b = 11.3292 (4) Å
c = 11.7601 (4) Å
α = 64.529 (1)°
β = 75.255 (2)°
γ = 81.149 (2)°
V = 883.73 (5) Å^3
Z = 2
$F(000)$ = 416
D_x = 1.532 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2661 reflections
θ = 6.0–64.6°
μ = 5.83 mm^{-1}
T = 296 K
Rectangle, yellow
0.27 × 0.24 × 0.22 mm

Data collection

Bruker X8 Proteum diffractometer
Radiation source: Bruker MicroStar microfocus rotating anode
Helios multilayer optics monochromator
Detector resolution: 18.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.302, T_{max} = 0.360
9181 measured reflections
2912 independent reflections
2661 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 64.6°, θ_{min} = 6.0°
h = −8→8
k = −13→13
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.152
S = 1.06
2912 reflections
226 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.106P)^2 + 0.5652P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.48103 (10)	0.67564 (8)	0.97162 (7)	0.0279 (3)
Cl2	0.38383 (13)	−0.08824 (8)	0.66214 (9)	0.0374 (3)
Cl3	0.10331 (10)	0.79457 (8)	0.07472 (7)	0.0318 (3)
S1	0.31946 (10)	0.19980 (7)	0.57645 (7)	0.0212 (2)
N1	0.2567 (3)	0.4921 (2)	0.5288 (2)	0.0193 (7)
N2	0.2453 (3)	0.6185 (2)	0.5214 (2)	0.0203 (8)
C1	0.3072 (4)	0.4138 (3)	0.6350 (3)	0.0185 (8)
C2	0.3445 (4)	0.4841 (3)	0.7088 (3)	0.0207 (9)
C3	0.2528 (4)	0.6197 (3)	0.6446 (3)	0.0181 (8)
C4	0.3357 (4)	0.2748 (3)	0.6743 (3)	0.0199 (9)
C5	0.3715 (4)	0.0492 (3)	0.6913 (3)	0.0241 (9)
C6	0.3988 (4)	0.0550 (3)	0.7975 (3)	0.0242 (9)
C7	0.3786 (4)	0.1844 (3)	0.7879 (3)	0.0215 (9)
C8	0.1945 (4)	0.7240 (3)	0.4180 (3)	0.0194 (8)
C9	0.1718 (4)	0.7085 (3)	0.3108 (3)	0.0203 (9)
C10	0.1291 (4)	0.8178 (3)	0.2075 (3)	0.0249 (9)
C11	0.1064 (4)	0.9423 (3)	0.2034 (3)	0.0282 (10)
C12	0.1267 (4)	0.9567 (3)	0.3110 (3)	0.0278 (10)
C13	0.1690 (4)	0.8507 (3)	0.4173 (3)	0.0228 (9)
C14	0.0662 (4)	0.6366 (3)	0.7233 (3)	0.0185 (8)
C15	−0.0936 (4)	0.6215 (3)	0.6946 (3)	0.0210 (9)
C16	−0.2608 (4)	0.6325 (3)	0.7706 (3)	0.0231 (9)
C17	−0.2694 (4)	0.6589 (3)	0.8767 (3)	0.0206 (8)
C18	−0.1130 (4)	0.6748 (3)	0.9073 (3)	0.0231 (9)
C19	0.0545 (4)	0.6625 (3)	0.8308 (3)	0.0229 (9)
H2A	0.47410	0.48940	0.69850	0.0250*
H2B	0.28980	0.44210	0.79980	0.0250*
H3	0.33100	0.68840	0.62950	0.0220*
H6	0.42730	−0.01750	0.86840	0.0290*
H7	0.39300	0.20660	0.85240	0.0260*
H9	0.18540	0.62610	0.30930	0.0240*
H11	0.07860	1.01400	0.13160	0.0340*
H12	0.11150	1.03970	0.31130	0.0330*
H13	0.18080	0.86250	0.48850	0.0270*
H15	−0.08740	0.60380	0.62340	0.0250*

H16	−0.36690	0.62240	0.75100	0.0280*
H18	−0.12020	0.69340	0.97810	0.0280*
H19	0.16040	0.67160	0.85140	0.0270*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0218 (4)	0.0380 (5)	0.0211 (4)	0.0026 (3)	−0.0010 (3)	−0.0129 (3)
Cl2	0.0569 (6)	0.0207 (4)	0.0377 (5)	−0.0023 (4)	−0.0138 (4)	−0.0127 (4)
Cl3	0.0274 (4)	0.0462 (5)	0.0197 (4)	0.0043 (3)	−0.0075 (3)	−0.0121 (4)
S1	0.0242 (4)	0.0200 (4)	0.0193 (4)	−0.0007 (3)	−0.0058 (3)	−0.0074 (3)
N1	0.0179 (12)	0.0210 (13)	0.0180 (13)	0.0001 (10)	−0.0027 (10)	−0.0080 (11)
N2	0.0262 (14)	0.0202 (13)	0.0127 (12)	0.0006 (10)	−0.0036 (10)	−0.0059 (10)
C1	0.0161 (14)	0.0212 (15)	0.0160 (15)	−0.0008 (11)	−0.0022 (11)	−0.0064 (12)
C2	0.0214 (15)	0.0215 (15)	0.0189 (16)	0.0025 (12)	−0.0060 (12)	−0.0083 (13)
C3	0.0199 (15)	0.0204 (14)	0.0148 (15)	−0.0017 (12)	−0.0055 (12)	−0.0067 (12)
C4	0.0165 (14)	0.0247 (16)	0.0185 (15)	−0.0003 (12)	−0.0017 (11)	−0.0102 (13)
C5	0.0221 (16)	0.0210 (15)	0.0261 (17)	0.0002 (12)	−0.0029 (13)	−0.0084 (13)
C6	0.0228 (16)	0.0230 (16)	0.0214 (16)	−0.0002 (13)	−0.0037 (12)	−0.0049 (13)
C7	0.0215 (15)	0.0245 (15)	0.0181 (15)	−0.0003 (12)	−0.0039 (12)	−0.0089 (13)
C8	0.0133 (14)	0.0238 (15)	0.0166 (15)	−0.0030 (11)	−0.0002 (11)	−0.0052 (12)
C9	0.0142 (14)	0.0251 (15)	0.0195 (16)	−0.0001 (12)	−0.0015 (12)	−0.0087 (13)
C10	0.0152 (15)	0.0386 (18)	0.0151 (15)	−0.0025 (13)	−0.0019 (12)	−0.0059 (13)
C11	0.0249 (17)	0.0293 (17)	0.0219 (17)	−0.0021 (13)	−0.0052 (13)	−0.0022 (14)
C12	0.0255 (17)	0.0224 (16)	0.0289 (18)	−0.0014 (13)	−0.0061 (14)	−0.0042 (14)
C13	0.0213 (15)	0.0253 (16)	0.0211 (16)	−0.0032 (12)	−0.0058 (12)	−0.0075 (13)
C14	0.0226 (15)	0.0162 (14)	0.0145 (14)	−0.0012 (11)	−0.0040 (12)	−0.0041 (12)
C15	0.0237 (16)	0.0259 (16)	0.0151 (15)	−0.0017 (12)	−0.0036 (12)	−0.0102 (13)
C16	0.0190 (15)	0.0311 (16)	0.0217 (16)	−0.0018 (13)	−0.0080 (12)	−0.0109 (13)
C17	0.0182 (15)	0.0202 (14)	0.0170 (15)	0.0013 (12)	−0.0007 (12)	−0.0041 (12)
C18	0.0278 (17)	0.0261 (16)	0.0166 (15)	−0.0005 (13)	−0.0027 (12)	−0.0113 (13)
C19	0.0227 (16)	0.0276 (16)	0.0196 (16)	−0.0025 (13)	−0.0070 (12)	−0.0090 (13)

Geometric parameters (Å, º)

Cl1—C17	1.746 (3)	C12—C13	1.380 (5)
Cl2—C5	1.717 (4)	C14—C15	1.394 (5)
Cl3—C10	1.753 (3)	C14—C19	1.395 (5)
S1—C4	1.734 (4)	C15—C16	1.379 (5)
S1—C5	1.725 (3)	C16—C17	1.387 (5)
N1—N2	1.387 (3)	C17—C18	1.385 (5)
N1—C1	1.296 (4)	C18—C19	1.386 (5)
N2—C3	1.470 (4)	C2—H2A	0.9700
N2—C8	1.380 (4)	C2—H2B	0.9700
C1—C2	1.503 (5)	C3—H3	0.9800
C1—C4	1.435 (5)	C6—H6	0.9300
C2—C3	1.535 (5)	C7—H7	0.9300
C3—C14	1.519 (5)	C9—H9	0.9300

C4—C7	1.372 (5)	C11—H11	0.9300
C5—C6	1.347 (5)	C12—H12	0.9300
C6—C7	1.408 (5)	C13—H13	0.9300
C8—C9	1.400 (5)	C15—H15	0.9300
C8—C13	1.415 (5)	C16—H16	0.9300
C9—C10	1.378 (5)	C18—H18	0.9300
C10—C11	1.376 (5)	C19—H19	0.9300
C11—C12	1.392 (5)		

C4—S1—C5	90.38 (16)	C15—C16—C17	119.4 (3)
N2—N1—C1	107.8 (2)	Cl1—C17—C16	119.6 (2)
N1—N2—C3	111.9 (2)	Cl1—C17—C18	119.3 (3)
N1—N2—C8	121.2 (2)	C16—C17—C18	121.1 (3)
C3—N2—C8	125.6 (3)	C17—C18—C19	119.0 (3)
N1—C1—C2	113.2 (3)	C14—C19—C18	120.8 (3)
N1—C1—C4	123.5 (3)	C1—C2—H2A	112.00
C2—C1—C4	123.2 (3)	C1—C2—H2B	112.00
C1—C2—C3	101.5 (3)	C3—C2—H2A	111.00
N2—C3—C2	100.6 (3)	C3—C2—H2B	111.00
N2—C3—C14	113.1 (3)	H2A—C2—H2B	109.00
C2—C3—C14	112.4 (3)	N2—C3—H3	110.00
S1—C4—C1	121.9 (2)	C2—C3—H3	110.00
S1—C4—C7	110.9 (3)	C14—C3—H3	110.00
C1—C4—C7	127.2 (3)	C5—C6—H6	124.00
Cl2—C5—S1	119.45 (19)	C7—C6—H6	124.00
Cl2—C5—C6	127.1 (3)	C4—C7—H7	123.00
S1—C5—C6	113.5 (3)	C6—C7—H7	123.00
C5—C6—C7	111.6 (3)	C8—C9—H9	121.00
C4—C7—C6	113.6 (3)	C10—C9—H9	121.00
N2—C8—C9	120.8 (3)	C10—C11—H11	121.00
N2—C8—C13	120.3 (3)	C12—C11—H11	121.00
C9—C8—C13	118.9 (3)	C11—C12—H12	119.00
C8—C9—C10	118.6 (3)	C13—C12—H12	119.00
Cl3—C10—C9	117.3 (3)	C8—C13—H13	120.00
Cl3—C10—C11	119.0 (2)	C12—C13—H13	120.00
C9—C10—C11	123.7 (3)	C14—C15—H15	120.00
C10—C11—C12	117.3 (3)	C16—C15—H15	120.00
C11—C12—C13	121.5 (3)	C15—C16—H16	120.00
C8—C13—C12	120.0 (3)	C17—C16—H16	120.00
C3—C14—C15	122.0 (3)	C17—C18—H18	121.00
C3—C14—C19	119.1 (3)	C19—C18—H18	121.00
C15—C14—C19	118.9 (3)	C14—C19—H19	120.00
C14—C15—C16	120.7 (3)	C18—C19—H19	120.00

C5—S1—C4—C1	179.6 (3)	C2—C3—C14—C19	78.1 (4)
C5—S1—C4—C7	−0.2 (3)	S1—C4—C7—C6	0.0 (4)
C4—S1—C5—Cl2	−179.7 (2)	C1—C4—C7—C6	−179.7 (3)
C4—S1—C5—C6	0.3 (3)	Cl2—C5—C6—C7	179.6 (3)

C1—N1—N2—C3	−12.7 (3)	S1—C5—C6—C7	−0.3 (4)
C1—N1—N2—C8	179.9 (3)	C5—C6—C7—C4	0.2 (4)
N2—N1—C1—C2	−2.8 (3)	N2—C8—C9—C10	−177.1 (3)
N2—N1—C1—C4	−179.2 (3)	C13—C8—C9—C10	1.3 (5)
N1—N2—C3—C2	21.5 (3)	N2—C8—C13—C12	176.9 (3)
N1—N2—C3—C14	−98.6 (3)	C9—C8—C13—C12	−1.5 (5)
C8—N2—C3—C2	−171.7 (3)	C8—C9—C10—Cl3	179.6 (2)
C8—N2—C3—C14	68.2 (4)	C8—C9—C10—C11	−0.3 (5)
N1—N2—C8—C9	−6.9 (4)	Cl3—C10—C11—C12	179.6 (2)
N1—N2—C8—C13	174.7 (3)	C9—C10—C11—C12	−0.6 (5)
C3—N2—C8—C9	−172.5 (3)	C10—C11—C12—C13	0.4 (5)
C3—N2—C8—C13	9.1 (5)	C11—C12—C13—C8	0.6 (5)
N1—C1—C2—C3	15.8 (3)	C3—C14—C15—C16	177.5 (3)
C4—C1—C2—C3	−167.9 (3)	C19—C14—C15—C16	0.3 (5)
N1—C1—C4—S1	4.5 (5)	C3—C14—C19—C18	−178.1 (3)
N1—C1—C4—C7	−175.9 (3)	C15—C14—C19—C18	−0.8 (5)
C2—C1—C4—S1	−171.5 (2)	C14—C15—C16—C17	0.0 (5)
C2—C1—C4—C7	8.1 (5)	C15—C16—C17—Cl1	178.9 (3)
C1—C2—C3—N2	−20.6 (3)	C15—C16—C17—C18	0.2 (5)
C1—C2—C3—C14	99.9 (3)	Cl1—C17—C18—C19	−179.4 (3)
N2—C3—C14—C15	14.0 (5)	C16—C17—C18—C19	−0.7 (5)
N2—C3—C14—C19	−168.8 (3)	C17—C18—C19—C14	1.0 (5)
C2—C3—C14—C15	−99.1 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···Cl2^{i}	0.98	2.82	3.700 (4)	150

Symmetry code: (i) *x*, *y*+1, *z*.