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3-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)-1,5-di-2-thienylpentane-1,5-dione: centrosymmetric dimers formed by C—H···π(thiophene) hydrogen bonds

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Molecules of the title compound, $C_{23}H_{19}ClN_2O_2S_2$, are linked into cyclic centrosymmetric dimers by paired C—H···π(thiophene) hydrogen bonds.

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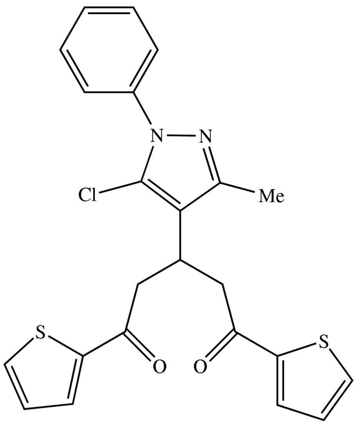
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.117
Data-to-parameter ratio = 17.5

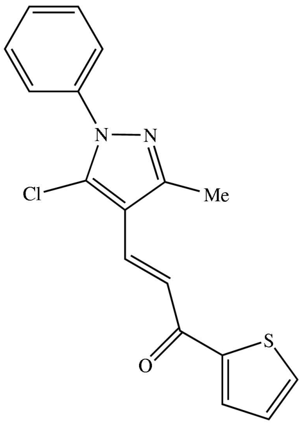
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), was obtained adventitiously during the attempted synthesis of the intermediate 3-(5-chloro-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl)-1-thiophen-2-yl-propenone, (II), by base-catalysed condensation of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde with 2-aceylthiophene. Evidently, the expected product, (II), has undergone a Michael-type reaction with a further mole of 2-acetylthiophene to form the observed product, (I).



(I)



(II)

Within the molecule of (I), the thiophene ring containing S9 exhibits orientational disorder about the C9—C91 bond, with occupancies of 0.623 (3) and 0.377 (3): all bond distances and angles show normal values.

The supramolecular aggregation is determined by C—H···π(thiophene) hydrogen bonds (Table 1). Atom C8 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the disordered thiophene ring of the molecule at (1 − *x*, 1 − *y*, 1 − *z*), so generating a centrosymmetric dimer (Fig. 2) whose formation is independent of the orientation of the thiophene acceptor (Table 1). The only other possible intermolecular interaction is a fairly short contact between atom Cl5 in the molecule at (*x*, *y*, *z*) and aryl atom C14 in the molecule at ($\frac{1}{2}+x$, y, $\frac{3}{2}-z$), with a Cl···C distance of 3.137 (2) Å and a C—Cl···C angle of 153.5 (2)°; this distance is not particularly short in terms of the polar flattening model for van der Waals contacts (Nyburg & Faerman, 1985) and is probably not structurally significant.

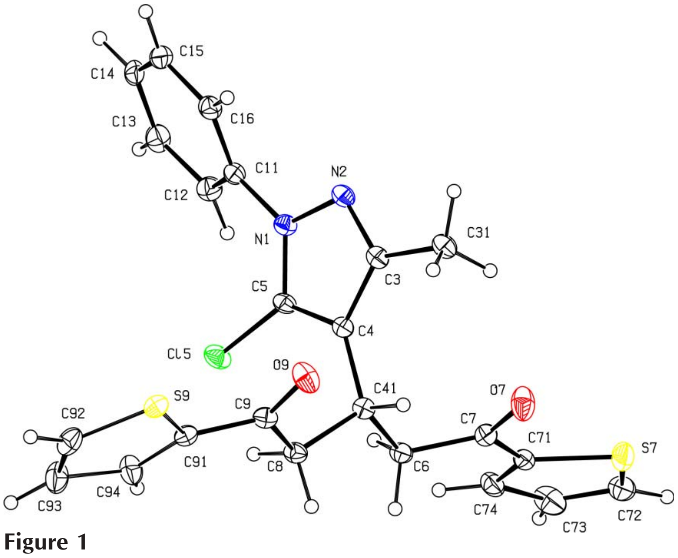


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only the major orientation of the disordered thiophene ring is shown.

Experimental

To a solution of 5-chloro-4-formyl-3-methyl-1-phenylpyrazole (0.5 mmol) and 2-acetylthiophene (1 mmol) in absolute ethanol (10 ml), a catalytic amount of sodium hydroxide (1 pellet) was added and the reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was isolated by filtration, washed with ethanol, dried and finally recrystallized from dimethylformamide to give yellow crystals suitable for single-crystal X-ray diffraction. M.p. 573 K, yield 45%; MS (70 eV) *m*/*z* (%): 455 (2.6) (*M*+), 329 (42), 293 (20), 111 (100).

Crystal data

$C_{23}H_{19}ClN_2O_2S_2$
$M_r = 454.99$
Orthorhombic, *Pbca*
$a = 14.6729\ (5)$ Å
$b = 17.8962\ (6)$ Å
$c = 16.2619\ (3)$ Å
$V = 4270.2\ (2)$ Å^3
$Z = 8$
$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4887 reflections
$\theta = 3.0$–27.5°
$\mu = 0.40$ mm^{-1}
$T = 120\ (2)$ K
Lath, colourless
0.42 × 0.22 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.851$, $T_{\max} = 0.969$
35379 measured reflections
4887 independent reflections
3231 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 27.5°$
$h = -19 \rightarrow 16$
$k = -23 \rightarrow 23$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.117$
$S = 1.03$
4887 reflections
279 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.8758P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}

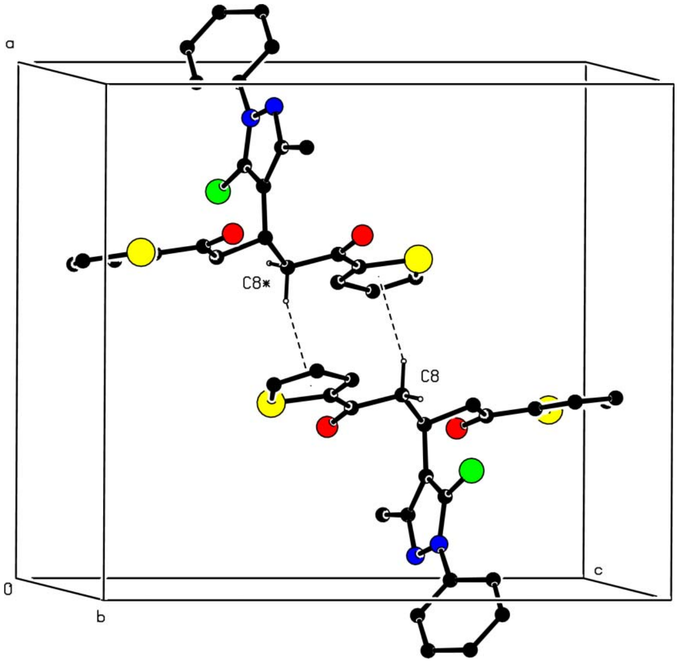


Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded dimer. For clarity, H atoms bonded to C atoms that are not involved in the motif shown have been omitted, and only the major orientation of the disordered thiophene ring is shown. Hydrogen bonds are shown as dashed lines. The atom marked with an asterisk (*) is at the symmetry position $(1 - x, 1 - y, 1 - z)$.

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

*Cg*1 and *Cg*2 are the centroids for the major and minor orientations of the disordered thiophene ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8*A*···*Cg*1$^{\rm i}$	0.99	2.67	3.628 (3)	162
C8—H8*A*···*Cg*2$^{\rm i}$	0.99	2.67	3.614 (3)	159

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

All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 Å (aromatic), 0.98 Å (CH_3), 0.99 Å (CH_2) or 1.00 Å (aliphatic CH), and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C), or $1.5U_{\rm eq}$(C) for the methyl group.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *WinGX* (Farrugia, 1999) and *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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