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Dimethyl 1-(3-chloro-4-methylphenyl)-pyrazole-3,4-dicarboxylate

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The dihedral angle between the phenyl and pyrazole moieties of the title compound, $C_{14}H_{13}ClN_2O_4$, is 8.66 (8)°. In the solid state, the symmetry-related molecules are linked by intermolecular C—H···O-type hydrogen bonds to form a continuous chain, which runs parallel to the c axis.

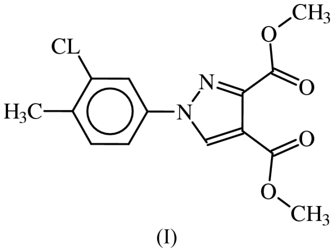
Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.116
Data-to-parameter ratio = 21.0

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

Comment

Studies on new classes of pharmaceuticals, agrochemicals and heterocycles are finding greater attention, because of their importance as precursors in the synthesis of pyrazolo-fused heterocycles (Hiremath *et al.*, 1995). Pyrazoles and their derivatives have been reported to show analgesic and anti-inflammatory activities (Liu *et al.*, 1998; Morimoto *et al.*, 1997). The present X-ray crystal structure analysis was undertaken in order to study the stereochemistry and crystal packing of the title compound, (I).



(I)

The bond lengths and angles in (I) are comparable to those found in related compounds (particularly, N2—N1—C5 > N1—N2—C3 and N2—C3—C4 > N1—C5—C4; Foces-Foces & Trofimenko, 2001). The widening of the exocyclic angles C4—C3—C13 [129.16 (13)°] and C3—C4—C16 [128.16 (13)°] from 120° may be due to the steric interaction between atoms O16 and O13 [O16···O13 = 3.006 (2) Å]. The dihedral angle between the phenyl and pyrazole moieties is 8.66 (8)°. The exocyclic angle C6—N1—C5 [128.28 (12)°] deviates significantly from the normal value (Lapasset & Falgueirettes, 1972). This may be due to the steric repulsion between atoms H5 of the pyrazole ring and H11 of the phenyl ring [H···H = 2.28 Å]. The dihedral angles between the pyrazole moiety and the 3,4-methoxycarbonyl groups are 38.86 (8) and 19.47 (7)°, respectively.

In the crystal structure, glide-related molecules are linked by intermolecular C—H···O-type hydrogen bonds (Table 2), having a binary graph-set motif of $R^1_2(7)$ (Bernstein *et al.*, 1995), to form a continuous chain, which runs parallel to the c axis.

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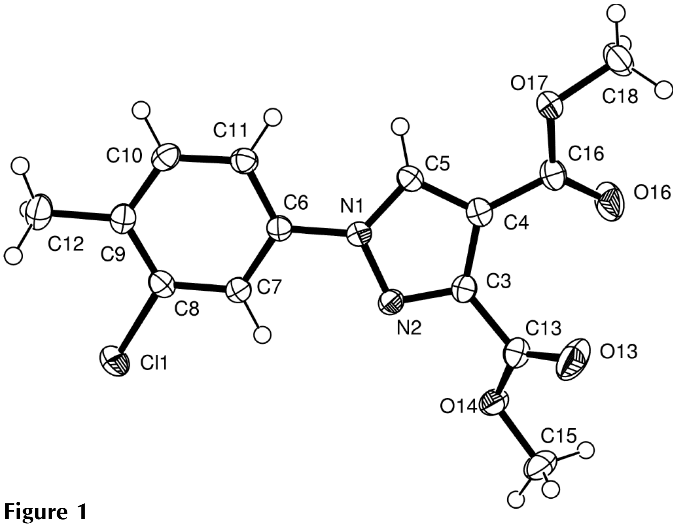

Figure 1
View of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii.

Experimental

To a solution of 3-(3-chloro-4-methylphenyl)sydnone (0.2105 g, 0.001 mol) in dry xylene (5 ml), dimethyl acetylene dicarboxylate (DMAD; 0.1563 g, 0.0011 mol) was added and the reaction mixture was refluxed for 2 h at 403 K. The solvent was removed *in vacuo* and the residue washed with petroleum ether. The resulting solid was crystallized from ethanol.

Crystal data

$C_{14}H_{13}ClN_2O_4$
$M_r = 308.72$
Monoclinic, $P2_1/c$
$a = 8.2279$ (1) Å
$b = 15.1992$ (2) Å
$c = 11.6764$ (2) Å
$\beta = 107.7807$ (7)°
$V = 1390.47$ (3) Å^3
$Z = 4$

$D_x = 1.475$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19230 reflections
$\theta = 2.0$–30.0°
$\mu = 0.29$ mm^{-1}
$T = 160$ (2) K
Tablet, colourless
0.30 × 0.28 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.877$, $T_{\max} = 0.943$
35568 measured reflections
4068 independent reflections

3039 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 30.0°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.117$
$S = 1.05$
4068 reflections
194 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.4477P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.011 (3)

Table 1
Selected geometric parameters (°).

C5—N1—N2	112.39 (11)	N1—C5—C4	106.72 (12)
C3—N2—N1	104.46 (11)	N2—C3—C4	111.55 (12)
C5—C4—C16—O16	−157.99 (16)	N2—C3—C13—O13	−137.36 (17)

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O16$^{\rm i}$	0.95	2.43	3.336 (2)	160
C11—H11···O16$^{\rm i}$	0.95	2.35	3.225 (2)	154

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

The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Version 1.07; Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

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