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

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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, C₁₄H₁₃ClN₂O₄, 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.

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).

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 R₁²(7) (Bernstein et al., 1995), to form a continuous chain, which runs parallel to the c axis.
Figure 1
View of the asymmetric unit of the title compound, showing the atom-labeling 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 was washed with petroleum ether. The resulting solid was crystallized from ethanol.

Crystal data
C14H13ClN2O4
Mr = 298.76
Monoclinic, P21/c
a = 8.2279 (1) Å
b = 15.1992 (2) Å
c = 11.6764 (2) Å
β = 107.7807 (7)°
V = 1390.47 (3) Å3
Z = 4

Data collection
Nonius KappaCCD diffractometer
β and ω scans with k offsets
Absorption correction: multi-scan
(Blessing, 1995)
Tmin = 0.877, Tmax = 0.943
35568 measured reflections
4068 independent reflections

Refinement
Refinement on F2
R[F2 > 2σ(F2)] = 0.041
wR(F2) = 0.117
S = 1.05
4068 reflections
194 parameters
H-atom parameters constrained

Table 1
Selected geometric parameters (°).

| C5—N1—N2 | 112.39 (11) |
| C3—N2—N1 | 104.46 (11) |
| C11—H11—O16 | 0.95 |
| C5—C4—C16—O16 | 157.99 (16) |

Symmetry code: (i) x, y, z + 2.

The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with Uiso(H) = 1.5Ueq(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 Uiso(H) = 1.2Ueq(C).

Data collection: COLLECT (Nonius, 2000); cell refinement: DENZO-SMN (Otwinski & Minor, 1997); data reduction: DENZO-SMN and SCALEPACK (Otwinski & Minor, 1997); program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: SHELX97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Version 1.07; Farrugia, 1997); software used to prepare material for publication: SHELX97 and PLATON (Spek, 2002).

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References