

Ethyl 3-methyl-1-(2,4-dinitrophenyl)-
1H-pyrazole-4-carboxylateS. Etti,^a G. Shanmugam,^a
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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.043

wR factor = 0.128

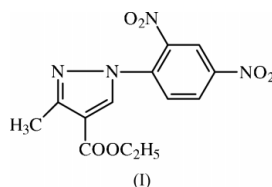
Data-to-parameter ratio = 12.5

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

The title compound, $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_6$, containing a dinitrophenyl ring substituted on the pyrazole ring, was obtained by a reaction of ethyl acetoacetate (2,4-dinitrophenyl)hydrazone with Vilsmeier reagent. The benzene and pyrazole rings are oriented at an angle of $35.49(6)^\circ$ with respect to each other. The packing of the molecules is controlled by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, in addition to van der Waals forces.

Comment

Pyrazoles find applications in medicine and the pharmaceutical industry. They possess biological activities, such as bacteriostatic, bacteriocidal, fungicidal, analgesic and antipyretic (Malhothra *et al.*, 1997; Potts, 1986). Some alkyl- and aryl-substituted pyrazoles have a sharply pronounced sedative action on the central nervous system (Vichlayev *et al.*, 1962; Raevskii & Batulin, 1963). The versatile pollen formation inhibitor activity (Richard & Wendellyn, 1986), herbicidal and insecticidal activities (Tutomu *et al.*, 1989; Susumu *et al.*, 1985) of 1H-pyrazole-4-carboxylic acid esters prompted us to carry out the crystal structure determination of the title compound, (I).



The bond lengths and angles in the pyrazole ring of (I) (Fig. 1 and Table 1) are comparable with those reported for similar pyrazole derivatives (Bonati & Bovio, 1990; Fronczek

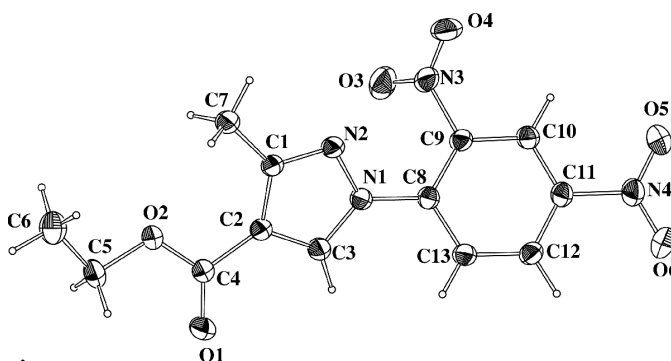


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

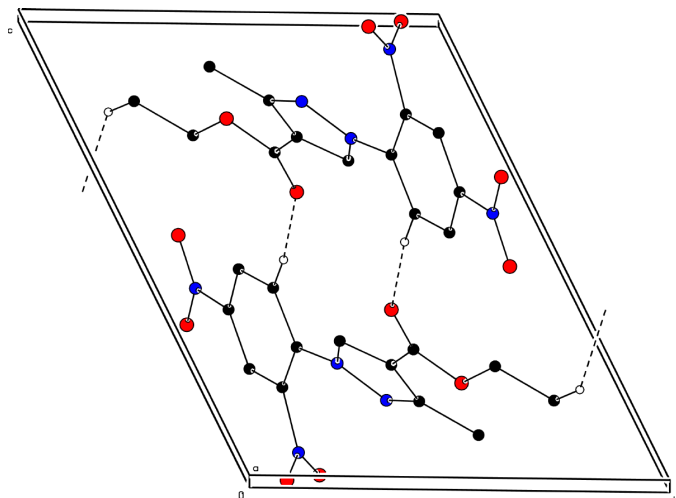


Figure 2
A view of the C—H···O hydrogen-bonded dimer.

et al., 1989; Jeyakanthan *et al.*, 1999; Mani Naidu *et al.*, 1996). The dihedral angle between the pyrazole and benzene rings, 35.49 (6)°, indicates imperfect conjugation.

The nitro group attached to the *ortho* position is twisted by an angle of 47.23 (7)° from the plane of the benzene ring. This twisting is due to the presence of a lone pair of electrons on atom N2 of the pyrazole ring, and indicates repulsion of the electron-rich O3 atom of the nitro group; the nitro group at the *para* position is almost coplanar [dihedral angle = 3.14 (6)°] with the ring. The ethoxycarbonyl group adopts an extended conformation, as evidenced by the torsion angles C5—O2—C4—C2 of −169.71 (14)° and C4—O2—C5—C6 of 166.06 (17)°.

The C5—C6 bond length of the ester group is shorter than the reported mean Csp^3-Csp^3 distance of 1.497 Å (Allen *et al.*, 1987).

In the crystal structure, inversion-related molecules form C—H···O hydrogen-bonded dimers (Fig. 2). The structure is further stabilized by C—H···O interactions between the dimers (Table 2). In addition, a C4···O6(2−x, 1−y, 1−z) short contact of 2.887 (2) Å and an O6···O6(3−x, 2−y, 1−z) short contact of 2.867 (2) Å are also observed in the structure.

Experimental

To an ice-cold stirred solution of ethyl acetoacetate (2,4-dinitrophenyl)hydrazone (0.31 g, 0.001 mol) in dry DMF (4 ml), 0.46 g of POCl₃ (0.003 mol) was added dropwise. The reaction mixture was allowed to attain room temperature and then refluxed at 343–353 K for about 4 h. The resulting mixture was poured on to crushed ice, neutralized with dilute sodium hydroxide and left standing overnight. The pale-yellow precipitate was purified by silica gel (60–120 mesh) column chromatography with an ethyl acetate–petroleum ether mixture (15:85) to yield the title compound (0.25 g), which was then recrystallized from a mixture of chloroform and methanol (1:1, *v/v*) by slow evaporation.

Crystal data

C₁₃H₁₂N₄O₆
 $M_r = 320.27$
 Triclinic, $P\bar{1}$
 $a = 7.7531$ (8) Å
 $b = 9.7146$ (10) Å
 $c = 11.4051$ (12) Å
 $\alpha = 113.649$ (2)°
 $\beta = 92.989$ (2)°
 $\gamma = 109.089$ (2)°
 $V = 726.74$ (13) Å³

$Z = 2$
 $D_x = 1.464$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 1829 reflections
 $\theta = 2.0$ – 28.0°
 $\mu = 0.12$ mm^{−1}
 $T = 293$ (2) K
 Block, pale yellow
 0.21 × 0.19 × 0.18 mm

Data collection

Bruker SMART APEX CCD area-detector
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.976$, $T_{\max} = 0.979$
 4623 measured reflections

3210 independent reflections
 2600 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\max} = 28.0^\circ$
 $h = -9 \rightarrow 10$
 $k = -9 \rightarrow 12$
 $l = -15 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.128$
 $S = 1.02$
 3210 reflections
 256 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2 + 0.0853P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.24$ e Å^{−3}
 $\Delta\rho_{\min} = -0.20$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

O1—C4	1.2097 (18)	N2—C1	1.3195 (19)
O2—C4	1.3282 (18)	C1—C2	1.424 (2)
O2—C5	1.451 (2)	C2—C3	1.367 (2)
N1—C3	1.3514 (19)	C2—C4	1.467 (2)
N1—N2	1.3749 (16)	C5—C6	1.490 (3)
N1—C8	1.4061 (19)		
C4—O2—C5	118.11 (13)	C3—C2—C1	105.48 (13)
C3—N1—N2	111.83 (12)	C3—C2—C4	124.67 (13)
C3—N1—C8	128.32 (12)	C1—C2—C4	129.62 (13)
N2—N1—C8	119.25 (11)	N1—C3—C2	106.80 (13)
C1—N2—N1	105.14 (11)	O1—C4—C2	123.86 (14)
N2—C1—C2	110.73 (12)	O2—C4—C2	111.60 (12)
N2—C1—C7	120.00 (13)	O2—C5—C6	106.50 (16)
C2—C1—C7	129.18 (14)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6A···O5 ⁱ	1.00 (4)	2.50 (3)	3.358 (3)	144 (2)
C13—H13···O1 ⁱⁱ	0.95 (2)	2.34 (2)	3.292 (2)	173 (2)

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

H-atom positions were located in a difference Fourier map and their positional and U_{iso} parameters were refined. The C—H distances are in the range 0.90 (3)–1.03 (2) Å.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ZORTEP (Zsolnai, 1997) and PLATON (Spek, 1990); software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1995).

SE gratefully acknowledges the award of a Professor R. Srinivasan Endowment Research Fellowship.

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