# organic papers

# Dimethyl 1-{4-[4,5-bis(methoxycarbonyl)-1,2,3-triazol-1-ylmethylcarbonyl]phenyl}-1H-pyrazole-3,4-dicarboxylate

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In the title molecule, $C_{21}H_{19}N_5O_9$, the dihedral angle between the mean planes of the triazole and pyrazole rings is 82.4 (1)°. In the solid state, symmetry-related molecules are linked by weak intermolecular C—H···O and C—H···N hydrogen bonds, having a graph-set motif of $R_2^2(10)$, to form chains running parallel to the $a$ axis.

## Comment

Azole derivatives, such as derivatives of pyrazole and triazole, have been reported to show analgesic and anti-inflammatory activities (Thamotharan *et al.*, 2003). The title compound, (I), is very useful in organic synthesis and compounds such as (I) are usually regarded as key synthons of oligomeric carboxamides, which are known to bind to DNA by lodging in the groove (Lee *et al.*, 1989; Chambers *et al.*, 1985). The present X-ray crystal structure analysis has been undertaken in order to study the stereochemistry and crystal packing of (I) (Fig. 1).



(I)
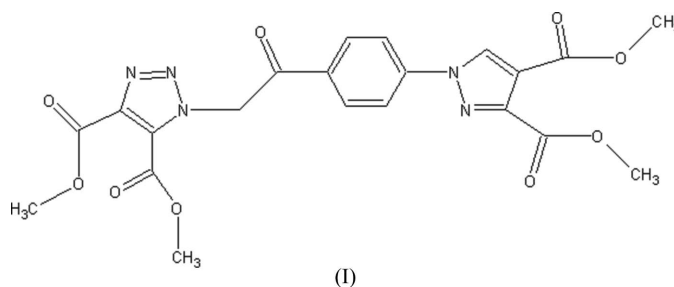
In (I), the bond lengths and angles of the phenyl-1H-pyrazole-3,4-dicarboxylate moiety are comparable with those found in two related structures, dimethyl 1-(3-chloro-4-methylphenyl)pyrazole-3,4-dicarboxylate (Thamotharan *et al.*, 2003), (II), and dimethyl 1-(7-acetoxy-4-methyl-2-oxo-2H-chromen-8-ylmethyl)-1H-pyrazole-3,4-dicarboxylate (Thamotharan *et al.*, 2004), (III). In all these three structures the following relations for the bond angles are fulfilled: C5—N1—N2 > C3—N2—N1 and N2—C3—C4 > N1—C5—C4. However, conformational differences are observed in the pyrazole-3,4-dicarboxylate groups of (I), (II) and (III). The least-squares fits between the pyrazole-3,4-dicarboxylate groups of (I) and (II) (Fig. 2a) and (I) and (III) (Fig. 2b) show deviations of 1.336 and 1.108 Å, respectively. The bond lengths and angles of the 1,2,3-triazole-4,5-dicarboxylate group are comparable with those found in two related structures, 5-amino-4-(2,6-dichlorophenyl)-1-(2-nitrophenyl)-1H-1,2,3-triazole (Sen & Venkatesan, 1984), (IV), and diethyl 1-(8-dimethylamino-1-naphthyl)-1H-1,2,3-triazole-4,5-dicarboxylate (Nagawa *et al.*, 1990), (V).
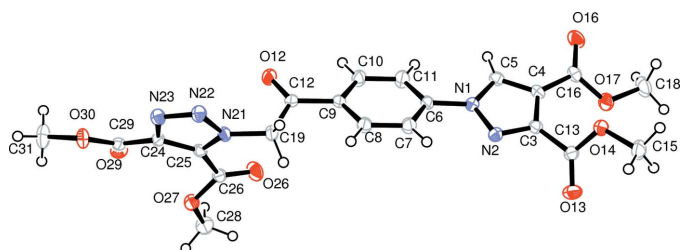
**Figure 1**
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radii.
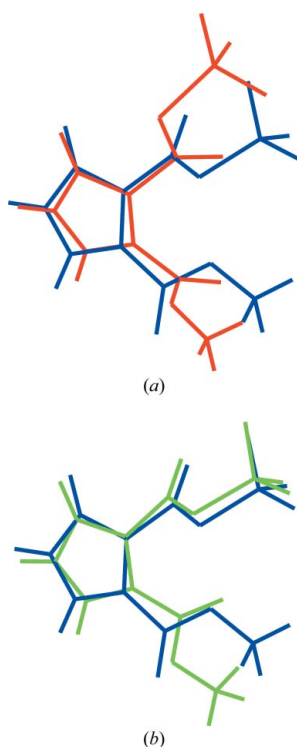


**Figure 2**
Superimposed fit between the pyrazole-3,4-dicarboxylate moieties of (a) (I) in blue and (II) in red, and (b) (I) in blue and (III) in green.

The triazole and pyrazole rings are nearly orthogonal, the dihedral angle between the mean planes of the rings being 82.4 (1)°. The dihedral angle between the mean planes of the pyrazole and benzene rings is 14.0 (1)°. The exocyclic angle C6—N1—C5 [128.41 (14)°] deviates significantly from the normal value (Lapasset & Falgueirettes, 1972). A similar deviation, 128.28 (12)°, is observed in (II). This deviation may be due to the steric repulsion between atom H5 of the pyrazole ring and atom H11 of the benzene ring (H···H = 2.36 Å). The widening of the exocyclic angles C13—C3—C4 [129.98 (14)°] and C3—C4—C16 [129.31 (15)°] from 120° may be due to the steric interaction between atoms O14 and O17 [O14···O17 = 2.957 (2) Å]. The dihedral angles between the pyrazole ring and the two 3,4-methoxycarbonyl groups are 53.9 (1) and 22.8 (1)°.

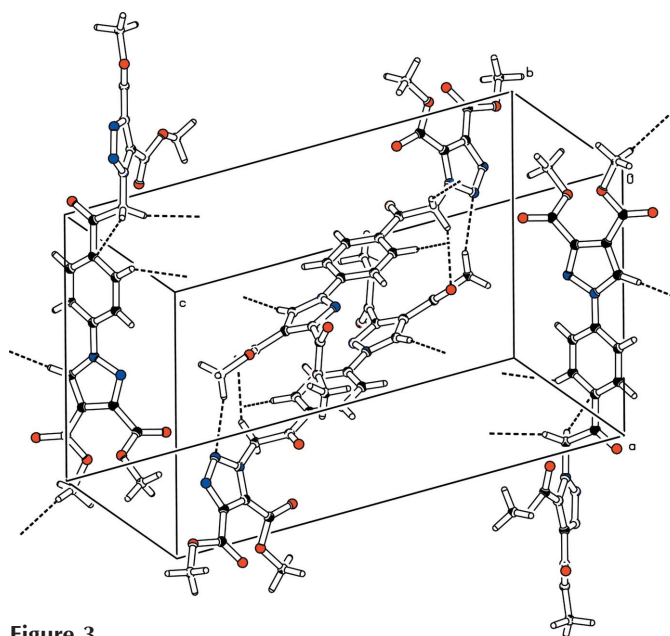The dihedral angle between the mean planes of the triazole and benzene rings is 68.3 (0)°. The torsion angles C25—C24—



**Figure 3**
The crystal packing, with the intermolecular hydrogen bonds shown as dashed lines.

C29—O30 [166.06 (15)°] and C24—C25—C26—O27 [−25.0 (2)°] show that the two carbonyl groups are twisted on opposite sides of the mean plane of the triazole ring. A similar observation has been made for structure (V). The dihedral angles between the mean planes of the triazole ring and 4,5-methoxycarbonyl groups are 19.6 (1) and 25.8 (1)°.

In (I), atom C19 acts as a donor for a weak intermolecular C—H···N interaction with atom N23 of the triazole ring of an adjacent molecule. Atom C8 is involved in a weak intermolecular C—H···O interaction with carboxyl atom O30 of an adjacent molecule. The symmetry-related molecules are linked by intermolecular C—H···O and C—H···N hydrogen bonds (Table 1), having a graph-set motif of $R_2^2(10)$ (Bernstein et al., 1995) (Fig. 3), to form a continuous chain, which runs parallel to the a axis.

## Experimental

A solution of 1-[4-(2-azido-acetyl)-phenyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (0.005 mol) in dry xylene (4 ml) was treated with dimethyl acetylenedicarboxylate (0.005 mol), and the reaction mixture was heated at 373 K till the evolution of carbon dioxide ceased (approximately 1 h). The solvent was removed under reduced pressure to obtain a yellow solid, which was recrystallized from dry benzene.

*Crystal data*

| | |
|---|---|
| $C_{21}H_{19}N_5O_9$ | $D_x = 1.457$ Mg m$^{-3}$ |
| $M_r = 485.41$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 10027 |
| $a = 12.0798$ (12) Å | reflections |
| $b = 8.5500$ (6) Å | $\theta = 3.7$–25.8° |
| $c = 21.424$ (2) Å | $\mu = 0.12$ mm$^{-1}$ |
| $\beta = 90.070$ (9)° | $T = 173$ (2) K |
| $V = 2212.7$ (4) Å$^3$ | Block, yellow |
| $Z = 4$ | $0.32 \times 0.30 \times 0.28$ mm |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| C19—H19$A\cdots$N23$^i$ | 0.99 | 2.46 | 3.316 (2) | 144 |
| C8—H8$\cdots$O30$^i$ | 0.95 | 2.54 | 3.322 (2) | 140 |
| C18—H18$C\cdots$N22$^{ii}$ | 0.98 | 2.59 | 3.540 (3) | 164 |
| C19—H19$B\cdots$O16$^{ii}$ | 0.99 | 2.54 | 3.426 (2) | 149 |
| C5—H5$\cdots$O29$^{iii}$ | 0.95 | 2.35 | 3.285 (2) | 168 |

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z + 1$.

All H atoms were treated as riding [C—H = 0.93–0.99 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H and $U_{iso}(H) = 1.2 U_{eq}(C)$ for others]. A short intermolecular contact, with a distance of 2.874 (2) Å, is observed between the atoms O13 and C29$^{iv}$ [symmetry code: (iv) $-1 + x, 1 + y, z$]. The structure was found to be twinned as pseudo-orthorhombic, with a 0.514 (1) contribution for the major component. 15 systematic violations were indicated by the *SHELXS97* (Sheldrick, 1997) program. These violations may be due to the twinning of the crystal. The reflection 109 was a strong reflection, which should have been systematically absent. However, the crystal structure was refined in the space group $P2_1/c$ only,

rejecting all the reflections that showed systematic absence violations. Two other reflections, 029 and $\bar{6}69$, were omitted.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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