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# Two polymorphic forms of 2,5-bis(4-methoxycarbonylphenyl)-1,3,4-oxadiazole

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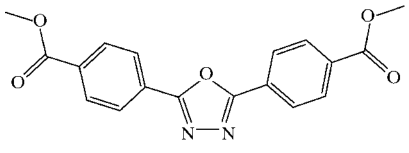
The title compound [systematic name: dimethyl 4,4′-(1,3,4-oxadiazole-2,5-diyl)diphenylenedicarboxylate], $C_{18}H_{14}N_2O_5$, crystallizes under similar conditions in two different orthorhombic crystalline forms. In both forms, the molecule consists of two equivalent parts. In form 1, these parts are related by a twofold axis of space group *Pbcn*, and in form 2, by a mirror plane of space group *Cmc*$2_1$. The O atom of the oxadiazole ring occupies a special position on the twofold axis and on the mirror plane in forms 1 and 2, respectively.

## Comment

Compounds containing a 1,3,4-oxadiazole ring as a basic building block are known as scintillator materials and as biologically active agents. Modifications of the chemical structures of these compounds open up possibilities for new technical applications, for instance, as potential electroluminiscent materials or as active sensor materials. In addition, the optical properties of these compounds should be taken into account, such as their potential for non-linear processes. In particular, polymers of 1,3,4-oxadiazoles exhibit interesting properties, including high thermal resistivity, good environmental stability, doping potential and mechanical toughness.



(I)

The title compound, (I), crystallizes in two different orthorhombic crystalline forms (Fig. 1). The molecule of form 1 is nearly planar; the dihedral angle between the central 1,3,4-oxadiazole ring and each of the phenyl rings is 4.64 (9)°, and the angle between a phenyl ring and its methoxycarbonyl group is 3.93 (9)°. The corresponding angles in form 2 are 8.86 (9) and 7.58 (8)°, respectively. However, in contrast to the molecule of form 1, the molecule of form 2 adopts a slightly bent shape. As shown in Fig. 2, the molecules in form 1 build up a herring-bone structure, with stacks extending along the *a* direction. Within the stacks, there are strong *π*–*π* interactions between adjacent molecular planes related by $a_o$ translations. The first plane formed by all of the non-H atoms of the molecule is defined by the equation $3.3409x - 0.0y + 18.7644z = 8.0320$, with an r.m.s. deviation of 0.0547 Å. The equation of the corresponding translated plane is $3.3409x - 0.0y + 18.7644z = 11.3730$. The distance between the two planes is 3.341 (3) Å. The molecular packing of form 2 is shown in Fig. 2.

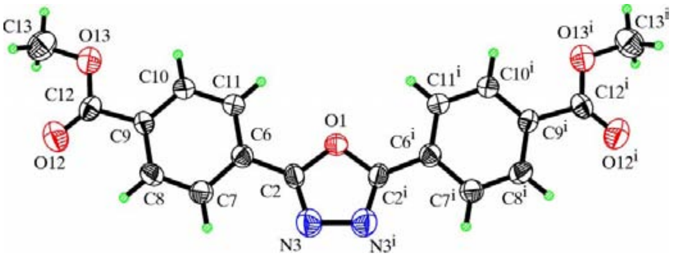


**Figure 1**
The molecular structure of (I), showing 50% probability displacement ellipsoids (*SHELXTL*; Sheldrick, 1999). H-atom labels have been omitted for clarity. [Symmetry code, for form 1: (i) $2 - x, y, \frac{1}{2} - z$; for form 2: (i) $-x, y, z$.]

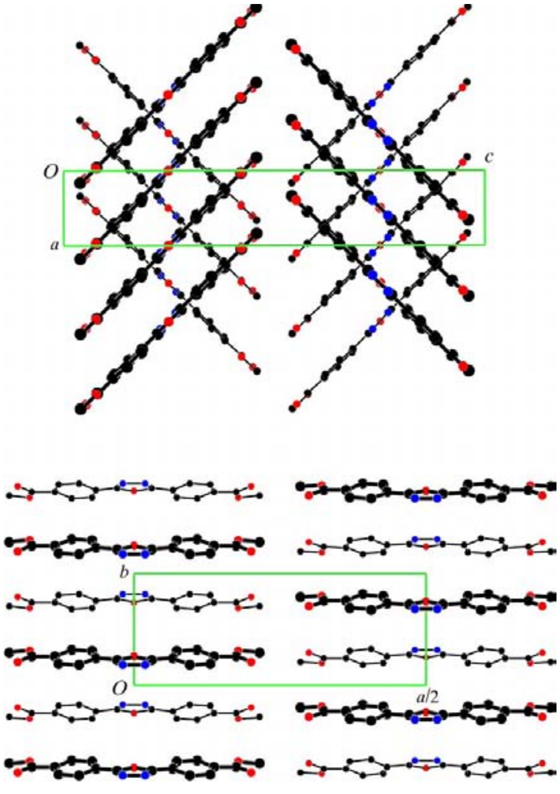


**Figure 2**
The molecular packing in form 1 (top) and form 2 (bottom).

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The packing is unlike that of form 1 in that no stacking interactions are found in form 2, as there are no molecules arranged parallel to one another. The angle between the planes of two neighbouring molecules related by a *c*-glide plane is 23.19 (3)°. The equations of the corresponding planes are $0.0x + 6.8316y + 1.2121z = 1.604$ and $0.0x - 6.8316y + 1.2121z = 2.2101$. The r.m.s. deviation about each plane is 0.1689 Å.

## Experimental

A mixture of dimethyl terephthalate (19.5 g) and hydrazine hydrate (5.57 g) was refluxed in methanol (500 ml) for 6 h. The resulting precipitate, *viz*. methyl terephthalate monohydrazide, was filtered off, dried and refluxed twice in chloroform (100 ml). The terephthalate monohydrazide (3 g) was stirred in absolute pyridine (50 ml), and methyl terephthalate chloride (3.07 g) in absolute tetrahydrofuran was added dropwise. The reaction mixture was stirred for 6 h at room temperature and then poured into a solution of water (600 ml) and HCl (50 ml, 37%). The pH of the solution was corrected to 5, and the precipitated solid product, *viz*. bis(4-methoxycarbonylbenzoyl)hydrazine, was filtered off, washed several times with water and dried. Bis(4-methoxycarbonylbenzoyl)hydrazine (4.8 g) was suspended in phosphoric acid chloride (50 ml) and a few drops of dimethylformamide (DMF) were added. The mixture was refluxed for 18 h and the product was precipitated in ice water. The title compound was recrystallized from DMF/ethanol (9:1), giving two different crystalline forms, as mentioned above.

### Form 1 of (I)

#### *Crystal data*

$C_{18}H_{14}N_2O_5$
$M_r = 338.31$
Orthorhombic, *Pbcn*
$a = 4.7350$ (10) Å
$b = 12.516$ (2) Å
$c = 26.480$ (3) Å
$V = 1569.3$ (5) Å$^3$
$Z = 4$
$D_x = 1.432$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–$20°$
$\mu = 0.11$ mm$^{-1}$
$T = 293$ (2) K
Needle, colourless
0.42 × 0.13 × 0.11 mm

#### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta$–$\omega$ scans
1394 measured reflections
1394 independent reflections
1052 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$

$h = 0 \rightarrow 5$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity decay: 0.5%

#### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.164$
$S = 1.10$
1394 reflections
115 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1156P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.024$
$\Delta\rho_{\max} = 0.40$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.39$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0065 (6)

### Form 2 of (I)

#### *Crystal data*

$C_{18}H_{14}N_2O_5$
$M_r = 338.31$
Orthorhombic, $Cmc2_1$
$a = 36.708$ (4) Å
$b = 6.9740$ (10) Å
$c = 6.0300$ (10) Å
$V = 1543.7$ (4) Å$^3$
$Z = 4$
$D_x = 1.456$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–$21°$
$\mu = 0.11$ mm$^{-1}$
$T = 293$ (2) K
Needle, colourless
0.39 × 0.11 × 0.10 mm

#### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta$–$\omega$ scans
1377 measured reflections
1377 independent reflections
1058 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$

$h = 0 \rightarrow 43$
$k = 0 \rightarrow 8$
$l = -7 \rightarrow 7$
3 standard reflections
frequency: 120 min
intensity decay: 0.3%

#### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 0.98$
1377 reflections
116 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.16$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0059 (6)

In the two crystalline forms of (I), the molecules consist of two equivalent parts, which are related by a twofold axis and by a mirror plane in forms 1 and 2, respectively. The O atoms of the oxadiazole rings occupy special positions. H-atom positions were calculated geometrically and refined using a riding model.

For both forms of (I), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1617). Services for accessing these data are described at the back of the journal.

## References

Enraf–Nonius (1977). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1999). *SHELXTL-NT*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.