

John N. Low,<sup>a</sup> Justo Cobo,<sup>b</sup> Jorge Trilleras<sup>c</sup> and Christopher Glidewell<sup>d\*</sup>

<sup>a</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, <sup>b</sup>Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, <sup>c</sup>Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, and <sup>d</sup>School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

#### Key indicators

Single-crystal X-ray study

$T = 120\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.047

$wR$  factor = 0.133

Data-to-parameter ratio = 17.3

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

## 2,5-Bis(4-methylphenyl)-7-phenyl-6,7-dihydro-pyrazolo[1,5-*a*]pyrimidine-3,6-dicarbaldehyde: hydrogen-bonded sheets built from N—H···O and C—H···O hydrogen bonds

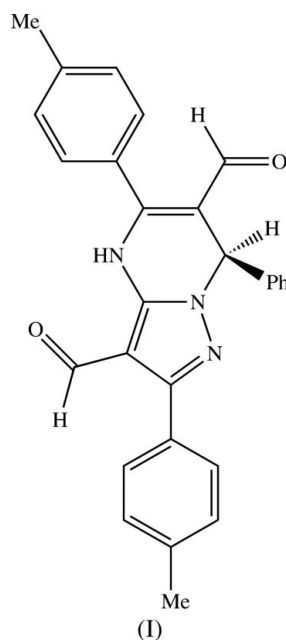
The molecules of the title compound,  $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_2$ , are linked into complex sheets by a combination of one N—H···O and two C—H···O hydrogen bonds.

Received 29 September 2006

Accepted 29 September 2006

### Comment

As part of a continuing search for biologically active molecules containing fused pyrazole systems, we have now prepared 2,5-bis(4-methylphenyl)-7-phenyl-6,7-dihydro-pyrazolo[1,5-*a*]pyrimidine-3,6-dicarbaldehyde, (I), of potential value as a precursor for modified or fused polycyclic pyrazolo[1,5-*a*]pyrimidine systems, and we report its structure here.



Within the molecule of (I), atom C7 is a stereogenic centre, and in the selected reference molecule this atom has the (*R*)-configuration; however, the space group accommodates equal numbers of (*R*) and (*S*) enantiomers. For the atom sequence C3A—N4—C5—C6—C7—N7A, the ring-puckering parameters (Cremer & Pople, 1975) are  $\theta = 70.2(5)^\circ$  and  $\varphi = 169.4(5)^\circ$ , indicating a ring conformation intermediate between boat [ $\theta = 90.0^\circ$ ,  $\varphi = (60k)^\circ$ , where  $k$  is zero or an integer] and screw-boat [ $\theta = 67.5^\circ$  and  $\varphi = (60k + 30)^\circ$ ]. While the aryl rings are all significantly twisted away from the mean plane of the heterocyclic core, as shown by the key torsion angles (Table 1), the two carboxaldehyde groups are nearly coplanar with the heterocycle. The short intramolecular N—H···O contact to O3 (Table 2) may contribute to this.

The molecules of (I) are linked into complex sheets by one N—H···O hydrogen bond and two C—H···O hydrogen bonds (Table 2), and the sheet formation is easily analysed in terms of two one-dimensional sub-structures. Atoms N4 and C73 in the molecule at  $(x, y, z)$  act as hydrogen-bond donors, respectively, to atoms O3 and O6 in the molecules at  $(2 - x, 1 - y, 1 - z)$  and  $(-x, 1 - y, -z)$ , respectively. Propagation by inversion of these two interactions then generates a chain of centrosymmetric rings running parallel to the  $[201]$  direction with  $R_2^2(16)$  (Bernstein *et al.*, 1995) rings centred at  $(2n, \frac{1}{2}, n)$  ( $n = \text{zero or an integer}$ ), and  $R_2^2(12)$  rings centred at  $(2n + 1, \frac{1}{2}, n + \frac{1}{2})$  ( $n = \text{zero or an integer}$ ) (Fig. 2). In addition, atom C74 in the molecule at  $(x, y, z)$  acts as a hydrogen-bond donor to atom O3 in the molecule  $(-1 + x, y, -1 + z)$ , so generating by translation a  $C(11)$  chain running parallel to the  $[101]$  direction (Fig. 3). The combination of the  $[101]$  and  $[201]$  chains generates a sheet parallel to  $(010)$  (Fig. 4).

## Experimental

A mixture of 5-amino-3-(4-methylphenyl)-1*H*-pyrazole (1.9 mmol) and 1-(4-methylphenyl)-3-phenylpropenone (1.9 mmol) in dimethylformamide (1 ml) was heated under reflux for 20 min, to afford the intermediate 2,5-di-(4-methylphenyl)-7-phenyl-6,7-dihydropyrazolo[1,5-*a*]pyrimidine. The reaction mixture was cooled to ambient temperature and the intermediate was collected by filtration, washed with ethanol and dried, and then purified by chromatography on alumina using chloroform as the eluent. Phosphoryl chloride (2.1 mmol) was then added dropwise to a suspension of the pyrazolopyrimidine intermediate (1.0 mmol) in dimethylformamide (2 ml) while cooling within an ice–water bath. When the addition had been completed the reaction mixture was stirred vigorously for 0.5 h at ambient temperature. The resulting solid product (I) was collected by filtration, dried and recrystallized from dimethylformamide to give yellow crystals suitable for single-crystal X-ray diffraction: yield 65%, m.p. 544 K; MS ( $m/z$ , %): 433 (92,  $M^+$ ), 356 (100), 91 (44), 65 (25).

### Crystal data

$C_{28}H_{23}N_3O_2$   
 $M_r = 433.49$   
 Monoclinic,  $P2_1/c$   
 $a = 10.4688$  (3) Å  
 $b = 22.3018$  (7) Å  
 $c = 11.0754$  (4) Å  
 $\beta = 118.723$  (2)°  
 $V = 2267.63$  (13) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.270$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Lath, yellow  
 $0.44 \times 0.40 \times 0.19$  mm

### Data collection

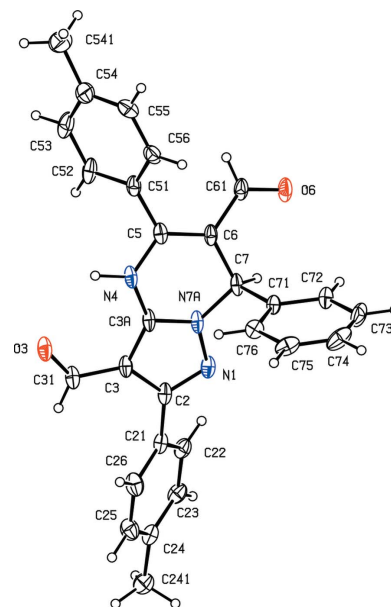
Bruker–Nonius KappaCCD  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.968$ ,  $T_{\max} = 0.986$

24100 measured reflections  
 5194 independent reflections  
 3286 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$   
 $\theta_{\text{max}} = 27.5^\circ$

### Refinement

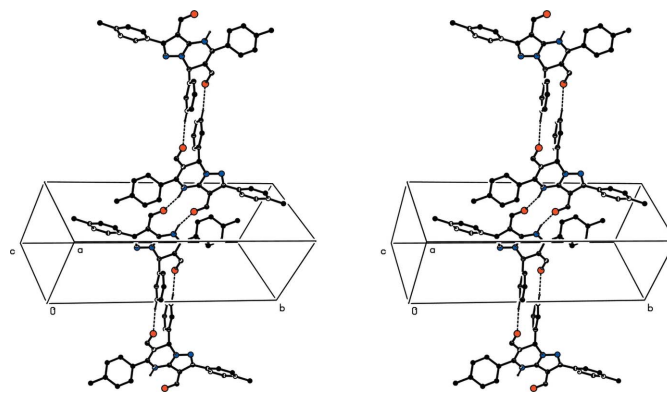
Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.133$   
 $S = 0.93$   
 5194 reflections  
 300 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.5212P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.032$   
 $\Delta\rho_{\text{max}} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.22$  e Å<sup>-3</sup>



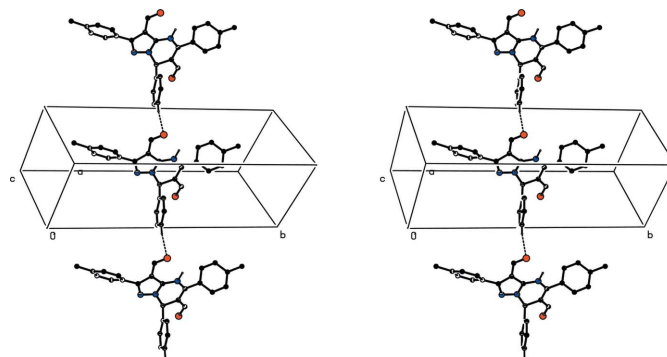
**Figure 1**

The molecular structure of the (*R*) enantiomer of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**

A stereoscopic view of part of the crystal structure of (I) showing the formation of a hydrogen-bonded chain of rings along  $[201]$ . Hydrogen bonds are shown as dashed lines, and for the sake of clarity the H atoms not involved in the motif shown have been omitted.



**Figure 3**

A stereoscopic view of part of the crystal structure of (I) showing the formation of a hydrogen-bonded chain along  $[101]$ . Hydrogen bonds are shown as dashed lines, and for the sake of clarity the H atoms not involved in the motif shown have been omitted.

**Table 1**Selected torsion angles ( $^{\circ}$ ).

N1—C2—C21—C22	-39.4 (2)	C3A—C3—C31—O3	-8.3 (3)
N4—C5—C51—C52	-54.56 (19)	C5—C6—C61—O6	-176.16 (15)
N7A—C7—C71—C72	137.35 (15)	C7—C6—C61—O6	-0.3 (2)

**Table 2**Hydrogen-bond geometry ( $\text{\AA}$ ,  $^{\circ}$ ).

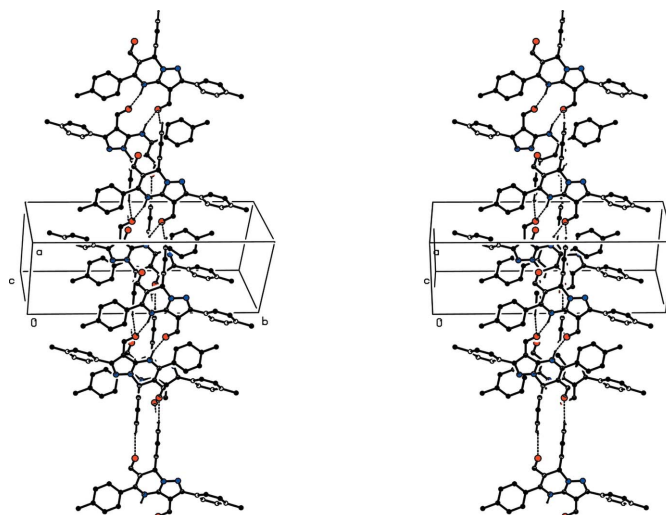
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4 $\cdots$ O3	0.98	2.36	2.933 (2)	117
N4—H4 $\cdots$ O3 <sup>i</sup>	0.98	2.02	2.968 (2)	163
C73—H73 $\cdots$ O6 <sup>ii</sup>	0.95	2.37	3.294 (3)	165
C74—H74 $\cdots$ O3 <sup>iii</sup>	0.95	2.44	3.376 (2)	170

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

All H atoms were located in difference maps and then treated as riding atoms with distances C—H 0.95  $\text{\AA}$  (aromatic and aldehydic), 0.98  $\text{\AA}$  (methyl) or 1.00  $\text{\AA}$  (aliphatic CH), and N—H 0.98  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C}, \text{N})$ , where  $k = 1.5$  for the methyl groups and 1.2 for all other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JT thanks COLCIENCIAS and UNIVALLE (Universidad del Valle, Colombia) for financial support.

**Figure 4**

A stereoscopic view of part of the crystal structure of (I) showing the formation of a hydrogen-bonded sheet parallel to (010). Hydrogen bonds are shown as dashed lines, and for the sake of clarity the H atoms not involved in the motif shown have been omitted.

## References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.