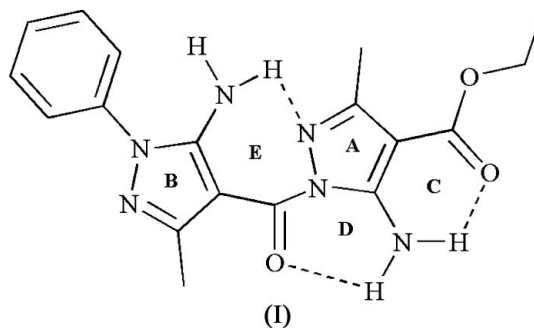


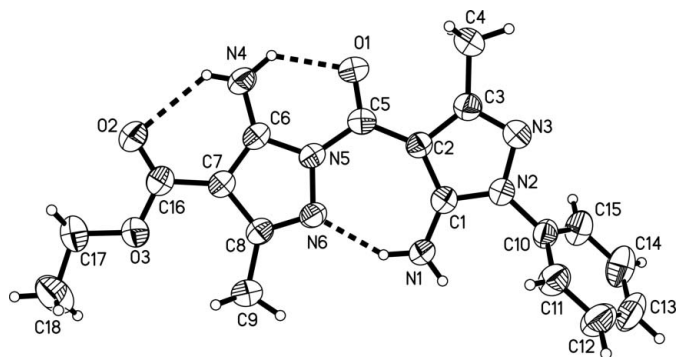
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of ChinaCorrespondence e-mail:  
lijunfei@mail.nankai.edu.cn**Key indicators**Single-crystal X-ray study  
 $T = 294$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.042  
 $wR$  factor = 0.116  
Data-to-parameter ratio = 14.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**Ethyl 5-amino-1-(5-amino-3-methyl-  
1-phenyl-1*H*-pyrazol-4-ylcarbonyl)-  
3-methyl-1*H*-pyrazole-4-carboxylate**The crystal structure of the title compound,  $\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_3$ , is  
stabilized by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds.Received 23 March 2006  
Accepted 26 March 2006**Comment**

4-Hydroxyphenylpyruvate dioxygenase (4-HPPD, EC1.1.3.11.27) is an important enzyme involved in the catabolism of tyrosine in most organisms and a relatively new target for herbicides. Since many benzoylpyrazole derivatives possess better herbicidal activity and belong to the inhibitor of this enzyme, they have received much more attention; these include pyrazolate (Yamaoka *et al.*, 1987, 1988), pyroxyfen (Kimura, 1984) and benzofenap (Kaoru *et al.*, 1991). All the compounds are pro-drugs for a shared active entity, the free hydroxypyrazole destosyl pyrazolate anion. It is also noted that NH and OH possess similar capabilities for forming hydrogen bonds, and both pyrazole and benzene rings are aromatic. However, herbicidal pyrazole derivatives containing two pyrazole rings have rarely been reported. This provides us with an opportunity of obtaining a herbicidal lead compound with two pyrazole rings containing amino groups. In this paper, we describe the crystal structure of the title compound, (I).



As shown in Fig. 1, the molecular structure of (I) is stabilized by three intramolecular hydrogen bonds (one  $\text{N}-\text{H}\cdots\text{N}$  and two  $\text{N}-\text{H}\cdots\text{O}$ ). The dihedral angles formed by rings A, B, C and E with ring D (all defined in the scheme) are 1.3 (1), 3.4 (1), 1.8 (1) and 2.7 (1) $^\circ$ , respectively, so they are practically coplanar.

Atom O1 forms an intramolecular hydrogen bond with atom H4D, not H1A, which may result from the steric hindrance of the benzene ring. The C1–N1 and C6–N4 distances are intermediate between a  $\text{C}=\text{N}$  double bond (C3=N3) and a C–N single bond (N2–C10). The C2–C5 and C16–C7 distances are intermediate between a  $\text{C}=\text{C}$

**Figure 1**

A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate the intramolecular hydrogen bonds.

double bond (C3=C2) and a C—C single bond (C3—C4). The bond lengths of rings A–E indicate extensive delocalization (Table 1). The crystal structure of (I) also involves a weak N—H···O hydrogen-bonding interaction (Fig. 2 and Table 2).

## Experimental

The title compound (I) was synthesized according to the procedure reported by Li *et al.* (2004). To a solution of ethyl (*Z*)-2-cyano-3-methoxybut-2-enoate (5.0 mmol) in ethanol (15 ml) was added 5-amino-3-methyl-1-phenyl-1*H*-pyrazole-4-carbohydrazide (5.5 mmol). The mixture was refluxed for 8 h and cooled to room temperature, then poured into water (30 ml). The white precipitate which formed was purified by recrystallization from ethanol–water (3:1 *v/v*). Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

### Crystal data

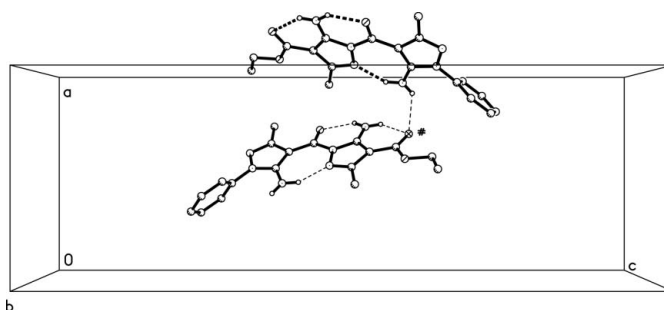
|   |                                       |
|---|---------------------------------------|
| C <sub>18</sub> H <sub>20</sub> N <sub>6</sub> O <sub>3</sub> | Mo K $\alpha$ radiation               |
| $M_r = 368.40$  | Cell parameters from 4591 reflections |
| Orthorhombic, $Pbca$  | $\theta = 2.8\text{--}24.3^\circ$     |
| $a = 10.5990$ (14) Å  | $\mu = 0.10$ mm <sup>-1</sup>         |
| $b = 10.9782$ (14) Å  | $T = 294$ (2) K                       |
| $c = 31.017$ (4) Å  | Block, colourless                     |
| $V = 3609.0$ (8) Å <sup>3</sup>                               | $0.42 \times 0.38 \times 0.28$ mm     |
| $Z = 8$   |                                       |
| $D_x = 1.356$ Mg m <sup>-3</sup>                              |                                       |

### Data collection

|  |  |
|--|--|
| Bruker SMART CCD area-detector diffractometer            | 3691 independent reflections           |
| $\varphi$ and $\omega$ scans                             | 2348 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1999) | $R_{\text{int}} = 0.041$               |
| $T_{\text{min}} = 0.956$ , $T_{\text{max}} = 0.973$      | $\theta_{\text{max}} = 26.4^\circ$     |
| 19243 measured reflections                               | $h = -13 \rightarrow 12$               |
|  | $k = -13 \rightarrow 13$               |
|  | $l = -26 \rightarrow 38$               |

### Refinement

|  |   |
|--|---|
| Refinement on $F^2$  | $w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.794P]$    |
| $R[F^2 > 2\sigma(F^2)] = 0.042$  | where $P = (F_o^2 + 2F_c^2)/3$                      |
| $wR(F^2) = 0.116$  | $(\Delta/\sigma)_{\text{max}} < 0.001$              |
| $S = 1.03$   | $\Delta\rho_{\text{max}} = 0.16$ e Å <sup>-3</sup>  |
| 3691 reflections   | $\Delta\rho_{\text{min}} = -0.18$ e Å <sup>-3</sup> |
| 263 parameters   |   |
| H atoms treated by a mixture of independent and constrained refinement |   |

**Figure 2**

A partial packing diagram for (I), showing the intra- and intermolecular hydrogen bonds as dashed lines. For the sake of clarity, H atoms bonded to C atoms have been omitted. The atom marked with a hash sign (#) is at the symmetry position  $(x - \frac{1}{2}, -y + \frac{1}{2}, -z)$ .

**Table 1**

Selected geometric parameters (Å, °).

|             |              |              |              |
|-------------|--------------|--------------|--------------|
| O1—C5       | 1.226 (2)    | N3—C3        | 1.312 (2)    |
| O2—C16      | 1.216 (2)    | N5—C6        | 1.383 (2)    |
| N1—C1       | 1.341 (2)    | N5—N6        | 1.3925 (19)  |
| N2—C1       | 1.351 (2)    | N5—C5        | 1.416 (2)    |
| N2—N3       | 1.388 (2)    | N6—C8        | 1.309 (2)    |
| N2—C10      | 1.427 (2)    |              |              |
|             |              |              |              |
| N1—C1—N2    | 120.66 (16)  | N4—C6—N5     | 124.10 (17)  |
| N1—C1—C2    | 133.05 (17)  | N4—C6—C7     | 129.30 (17)  |
| N2—C1—C2    | 106.28 (15)  | N5—C6—C7     | 106.60 (14)  |
| O1—C5—N5    | 115.31 (15)  | O2—C16—O3    | 122.92 (17)  |
| O1—C5—C2    | 121.62 (16)  | O2—C16—C7    | 124.15 (18)  |
| N5—C5—C2    | 123.08 (16)  | O3—C16—C7    | 112.91 (16)  |
|             |              |              |              |
| N1—C1—C2—C3 | −177.5 (2)   | N6—N5—C5—C2  | −0.8 (2)     |
| N2—C1—C2—C3 | 1.22 (18)    | C1—C2—C5—O1  | −174.70 (19) |
| N1—C1—C2—C5 | −0.3 (4)     | C3—C2—C5—O1  | 2.2 (3)      |
| N2—C1—C2—C5 | 178.42 (19)  | C1—C2—C5—N5  | 5.6 (3)      |
| C1—C2—C3—N3 | −0.5 (2)     | C3—C2—C5—N5  | −177.54 (16) |
| C5—C2—C3—N3 | −178.34 (16) | N4—C6—C7—C8  | 178.88 (18)  |
| C1—C2—C3—C4 | 179.4 (2)    | N5—C6—C7—C8  | −1.75 (18)   |
| C6—N5—C5—O1 | −2.1 (3)     | N4—C6—C7—C16 | 0.1 (3)      |
| N6—N5—C5—O1 | 179.49 (15)  | N5—C6—C7—C16 | 179.45 (15)  |
| C6—N5—C5—C2 | 177.60 (16)  |              |              |

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D\text{—}H\cdots A$     | $D\text{—}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{—}H\cdots A$ |
|--------------------------|--------------|-------------|-------------|----------------------|
| N4—H4E···O2              | 0.85 (2)     | 2.25 (2)    | 2.863 (3)   | 129.1 (18)           |
| N4—H4D···O1              | 0.92 (2)     | 1.96 (2)    | 2.630 (2)   | 128 (2)              |
| N1—H1B···O2 <sup>i</sup> | 0.84 (2)     | 2.64 (2)    | 3.319 (2)   | 139.2 (17)           |
| N1—H1A···N6              | 0.91 (2)     | 1.91 (2)    | 2.708 (2)   | 146.2 (19)           |

Symmetry code: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z$ .

N-bound H atoms were located in a difference Fourier map and refined freely. The remaining H atoms were positioned geometrically and treated as riding atoms, with C—H distances of 0.93 (CH), 0.96 (CH<sub>3</sub>) or 0.97 Å (CH<sub>2</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the CH and CH<sub>2</sub> groups or  $1.5U_{\text{eq}}(\text{C})$  for CH<sub>3</sub>.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

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