

**Bis(5-amino-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-  
3,4,5-trimethoxyphenylmethane: sheets built  
from N—H···N and N—H···O hydrogen bonds**John N. Low,<sup>a</sup> Justo Cobo,<sup>b</sup> Jaime Portilla,<sup>c</sup> Jairo Quiroga<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 Colombia, and <sup>d</sup>School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

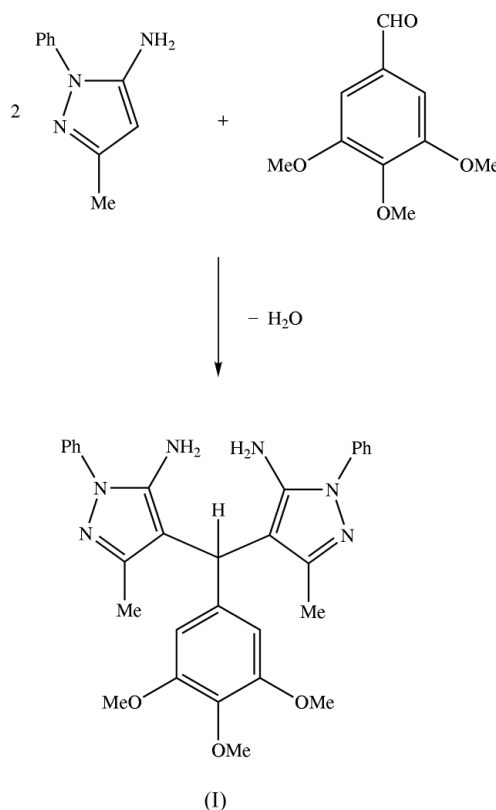
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**Key indicators**Single-crystal X-ray study  
*T* = 120 K  
Mean  $\sigma$ (C—C) = 0.003 Å  
Disorder in main residue  
*R* factor = 0.055  
*wR* factor = 0.144  
Data-to-parameter ratio = 12.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In molecules of the title compound, C<sub>30</sub>H<sub>32</sub>N<sub>6</sub>O<sub>3</sub>, there is an intramolecular N—H···N hydrogen bond [H···N = 2.28 Å, N···N = 3.194 (3) Å and N—H···N = 167°]. The molecules are linked by an N—H···O hydrogen bond [H···O = 2.37 Å, N···O = 3.255 (3) Å and N—H···O = 154°] into *C*(10) chains along [100], and by an intermolecular N—H···N hydrogen bond [H···N = 2.06 Å, N···N = 2.958 (3) Å and N—H···N = 155°] into *C*(8) chains along [001]; these chains combine to generate (010) sheets.

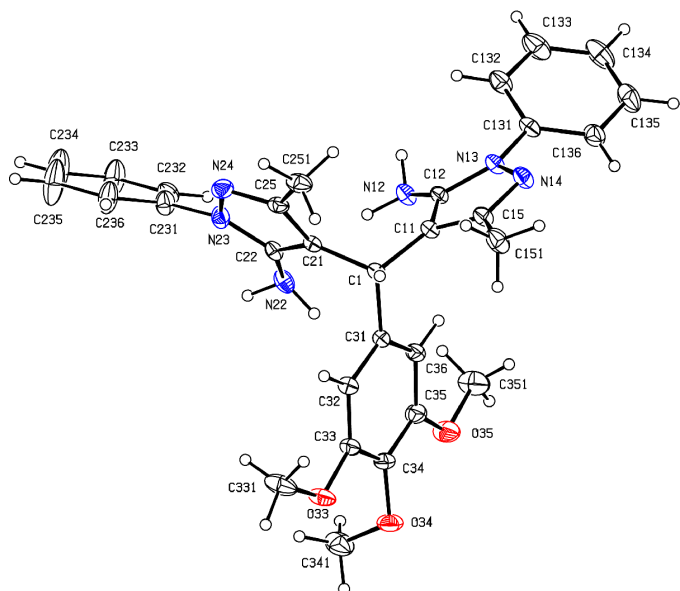
**Comment**

The title compound, (I) (Fig. 1), was obtained by microwave heating of a 2:1 molar ratio of 5-amino-3-methyl-1-phenyl-1*H*-pyrazole and 3,4,5-trimethoxybenzaldehyde in a solvent-free reaction (see scheme).



Although, in principle, molecules of (I) could adopt a conformation with mirror symmetry, in the event the key torsion angles (Table 1) defining the orientations of the two pyrazole rings relative to that of the trimethoxyphenyl unit preclude the possibility of any molecular symmetry. In addition, the phenyl ring bonded to N23 is disordered over at least

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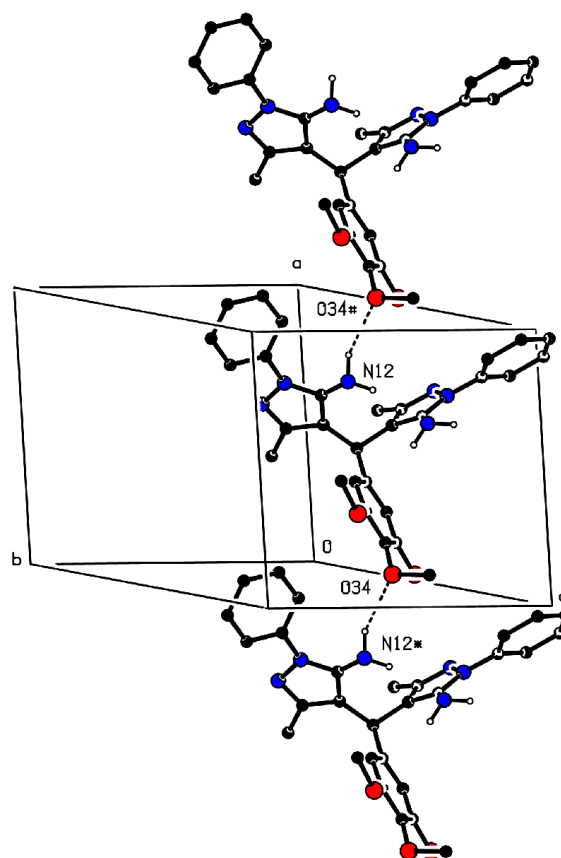
**Figure 1**  
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only one orientation of the disordered phenyl ring is shown.

two sites, while that bonded to N13 is fully ordered. This disorder, and the orientations of these phenyl rings relative to the adjacent pyrazole rings, also rule out any internal molecular symmetry. The molecules of (I) are accordingly chiral in the solid state, although this chirality probably has no chemical significance; however, the centrosymmetric space group accommodates equal numbers of the two enantiomers.

Within the trimethoxyphenyl unit, the methoxy groups based on O33 and O35 are almost coplanar with the adjacent benzene ring, whereas the C34–O34–C341 unit is nearly orthogonal to this ring. Associated with this difference, the exocyclic bond angles at C33 and C35 show the usual pattern of differences between the angles *cisoid* and *transoid* to the methyl group (Seip & Seip, 1973; Ferguson *et al.*, 1996; Patterson *et al.*, 1998; Abonia *et al.*, 2003), while the two exocyclic angles at C34 are nearly identical. In addition, the bond O34–C34 is marginally longer than the bonds O33–C33 and O35–C35, again a stereoelectronic consequence of the different conformations of the methoxy substituents.

The corresponding bond distances within the two independent pyrazole units are very similar, and all are typical of their types (Allen *et al.*, 1987): the C–C bonds connecting the central atom C1 to the pyrazole units are markedly shorter than that to the trimethoxyphenyl ring.

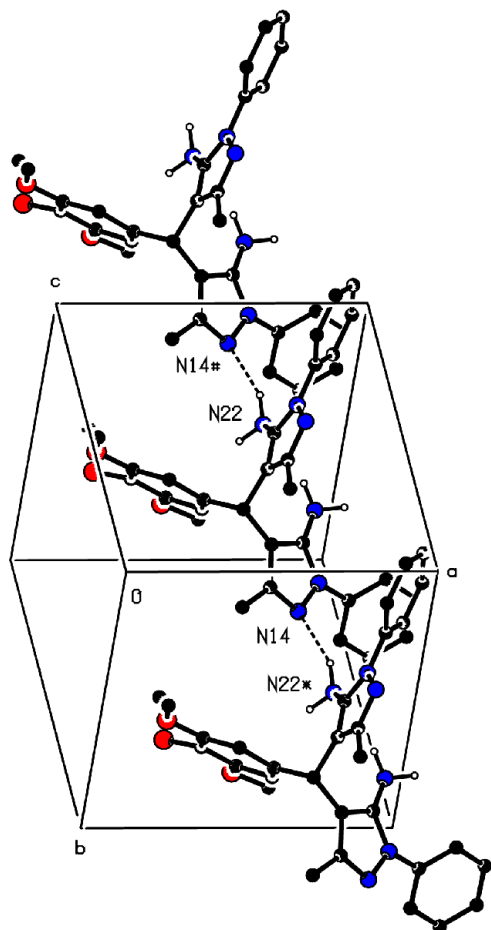
The amino atoms N12 and N22 act respectively as double and single donors of hydrogen bonds, while N22 in addition acts as a single acceptor (Table 2). Within the molecule, N12 acts as hydrogen-bond donor, *via* H12A, to atom N22, forming an *S*(8) motif (Bernstein *et al.*, 1995). Two intermolecular hydrogen bonds link the molecules into sheets, and the formation of the sheet is most readily analysed in terms of two simple one-dimensional substructures.



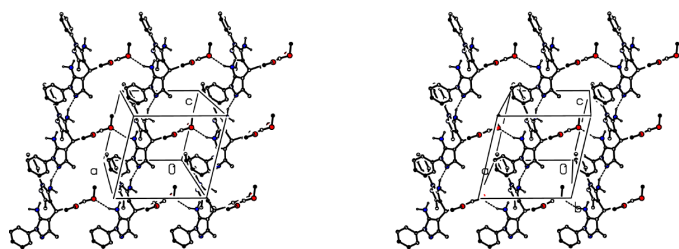
**Figure 2**  
Part of the crystal structure of compound (I), showing the formation of a *C*(10) chain along [100]. Atoms marked with an asterisk (\*) or a hash (#) are at the symmetry positions  $(x - 1, y, z)$  and  $(1 + x, y, z)$ , respectively. For the sake of clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered phenyl ring is shown.

Amino atom N12 in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor, *via* H12B, to methoxy atom O34 in the molecule at  $(1 + x, y, z)$ , generating by translation a *C*(10) chain running parallel to the [100] direction (Fig. 2). In the second substructure, amino atom N22 in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor, *via* H22A, to ring atom N14 in the molecule at  $(x, y, 1 + z)$ , thus generating by translation a *C*(8) chain running parallel to the [001] direction (Fig. 3). Atom N22 acts only as a single donor of hydrogen bonds, and there are no other potential acceptors within hydrogen-bonding distance. It may be noted here, firstly, that the intramolecular N–H...N hydrogen bond is likely to be an important influence on the overall molecular conformation and, secondly, that the pattern of the intermolecular hydrogen bonds is itself sufficient to preclude the possibility of any intramolecular symmetry.

The combination of the [100] and [001] chains generates a (010) sheet in the form of a (4,4)-net (Batten & Robson, 1998). Four sheets of this type pass through each unit cell, in the domains  $0 < y < 0.25$ ,  $0.25 < y < 0.50$ ,  $0.50 < y < 0.75$  and  $0.75 < y < 1.00$ , but there are no direction-specific interactions between adjacent sheets. In particular, despite the large number of O and N atoms available as potential acceptors of hydrogen bonds, there are no significant C–H...O or C–H...N


**Figure 3**

Part of the crystal structure of compound (I), showing the formation of a C(8) chain along [001]. Atoms marked with an asterisk (\*) or a hash (#) are at the symmetry positions  $(x, y, z - 1)$  and  $(x, y, 1 + z)$ , respectively. For the sake of clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered phenyl ring is shown.


**Figure 4**

Stereoview of part of the crystal structure of compound (I), showing the formation of a (010) sheet by combination of the [100] and [001] chains. For the sake of clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered phenyl ring is shown.

interactions in the structure and, despite the presence of three independent aryl rings, there are neither  $X-H \cdots \pi(\text{arene})$  hydrogen bonds ( $X = \text{C}$  or  $\text{N}$ ) nor aromatic  $\pi-\pi$  stacking interactions.

## Experimental

A mixture of 5-amino-3-methyl-1-phenyl-1*H*-pyrazole (1.16 mmol) and 3,4,5-trimethoxybenzaldehyde (0.58 mmol) was placed in an

open Pyrex-glass vessel and irradiated in a domestic microwave oven for 90 s at 600 W. The crude reaction product was crystallized from ethanol, yielding crystals of (I) suitable for single-crystal X-ray diffraction (yield 84%, m.p. 593 K). Analysis found: C 68.6, H 6.1, N 16.1%;  $\text{C}_{30}\text{H}_{32}\text{N}_6\text{O}_3$  requires C 68.7, H 6.1, N 16.0%.

## Crystal data

$\text{C}_{30}\text{H}_{32}\text{N}_6\text{O}_3$	$D_x = 1.234 \text{ Mg m}^{-3}$
$M_r = 524.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5973 reflections
$a = 9.7540 (2) \text{ \AA}$	$\theta = 2.8\text{--}27.5^\circ$
$b = 33.4646 (7) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 8.9010 (1) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 103.6020 (9)^\circ$	Lath, orange
$V = 2823.92 (9) \text{ \AA}^3$	$0.15 \times 0.10 \times 0.05 \text{ mm}$
$Z = 4$	

## Data collection

Nonius KappaCCD diffractometer	4968 independent reflections
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets	3683 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.081$
$T_{\text{min}} = 0.977, T_{\text{max}} = 0.996$	$\theta_{\text{max}} = 25.0^\circ$
25 815 measured reflections	$h = -11 \rightarrow 11$
	$k = -39 \rightarrow 39$
	$l = -10 \rightarrow 10$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 1.5741P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.144$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
4968 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
388 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

O33—C33	1.370 (2)	C1—C11	1.508 (3)
O34—C34	1.383 (3)	C1—C21	1.510 (3)
O35—C35	1.370 (3)	C1—C31	1.530 (3)
C11—C12	1.387 (3)	C21—C22	1.377 (3)
C12—N13	1.366 (3)	C22—N23	1.368 (3)
N13—N14	1.387 (3)	N23—N24	1.384 (3)
N14—C15	1.327 (3)	N24—C25	1.329 (3)
C15—C11	1.403 (3)	C25—C21	1.412 (3)
C12—N12	1.378 (3)	C22—N22	1.388 (3)
O33—C33—C32	124.6 (2)	O33—C33—C34	114.9 (2)
O34—C34—C33	120.1 (2)	O34—C34—C35	119.8 (2)
O35—C35—C34	116.0 (2)	O35—C35—C36	124.3 (2)
C31—C1—C11—C12	83.3 (3)	C31—C1—C21—C22	−37.3 (3)
C331—O33—C33—C32	8.6 (3)	C351—O35—C35—C36	−6.5 (4)
C341—O34—C34—C33	85.8 (3)	C12—N13—C131—C132	45.9 (3)
C22—N23—C231—C232	−35.9 (5)	C22—N23—C23A—C23B	−63.5 (4)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N12—H12A $\cdots$ N22	0.93	2.28	3.194 (3)	167
N12—H12B $\cdots$ O34 <sup>i</sup>	0.95	2.37	3.255 (3)	154
N22—H22A $\cdots$ N14 <sup>ii</sup>	0.96	2.06	2.958 (3)	155

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

All H atoms were located in difference maps and those bonded to carbon were then treated as riding atoms, with distances C—H = 0.95 (aromatic), 0.98 (methyl) or 1.00  $\text{\AA}$  (aliphatic CH), and with  $U_{\text{iso}}(\text{H}) =$

$1.2U_{\text{eq}}(\text{C})$ , or  $1.5U_{\text{eq}}(\text{C})$  for the methyl groups. The H atoms bonded to nitrogen were allowed to ride on their parent atoms at the distances deduced from the difference maps, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ ; the N–H distances were in the range 0.93–0.96 Å. It became apparent at an early stage that the phenyl ring bonded to N23 was disordered. When this was modelled using two sets of atom sites, the refined occupancies of the two sets were identical within experimental uncertainty, and hence they were subsequently fixed at 0.50. There is some indication from the displacement parameters that this ring might, indeed, be disordered over more than two sites, although no static disorder model could be found which was superior to the two-site model. Nonetheless, it was found desirable to treat both components of this disordered ring as planar rigid hexagons.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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).

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