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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

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.055
wR factor = 0.144
Data-to-parameter ratio = 12.8

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

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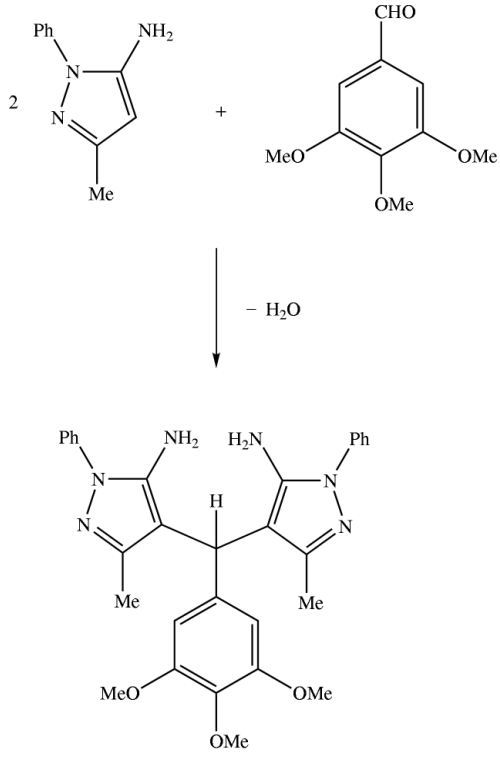
In molecules of the title compound, $C_{30}H_{32}N_6O_3$, there is an intramolecular N—H···N hydrogen bond [H···N = 2.28 Å, N···N = 3.194 (3) Å and N—H···N = 167°]. The molecules are linked by an N—H···O hydrogen bond [H···O = 2.37 Å, N···O = 3.255 (3) Å and N—H···O = 154°] into *C*(10) chains along [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).



(I)

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

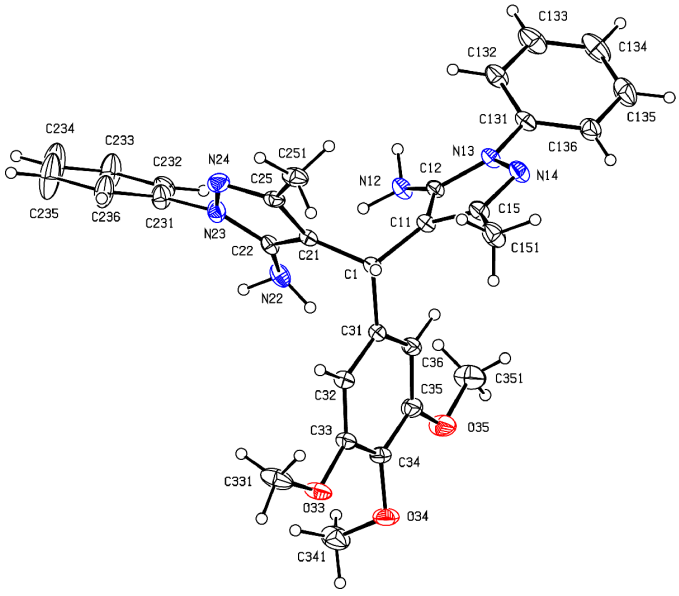


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only one orientation of the disordered phenyl ring is shown.

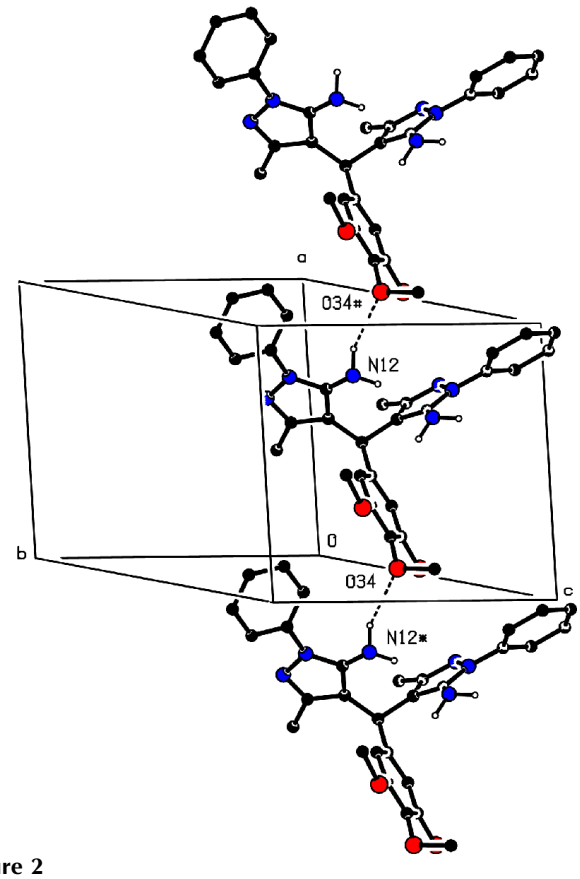


Figure 2
Part of the crystal structure of compound (I), showing the formation of a $C(10)$ chain along [100]. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x-1, y, z)$ and $(1+x, y, z)$, respectively. For the sake of clarity, H atoms bonded to C atoms have been omitted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

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.

Amino atom N12 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* H12*B*, 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* H22*A*, 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 three 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 $0.75 < 1.00$, 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

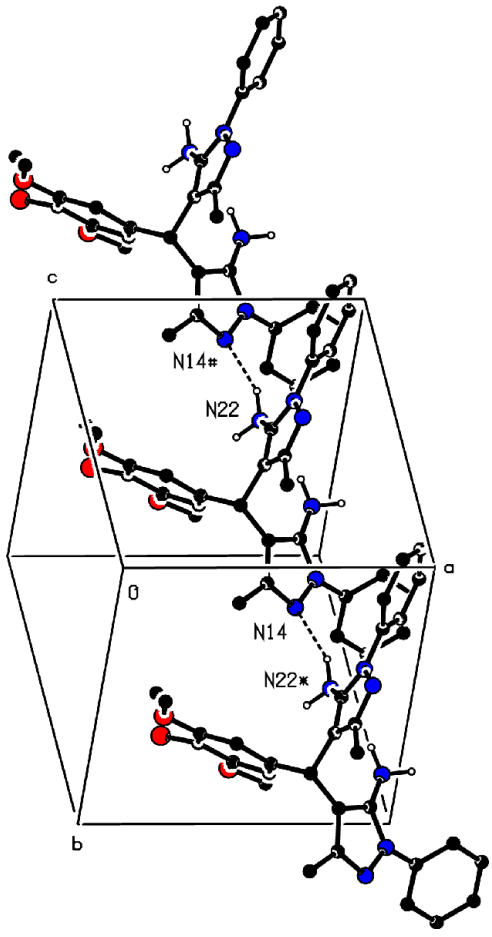


Figure 3
Part of the crystal structure of compound (I), showing the formation of a $C(8)$ chain along [001]. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y, z-1)$ and $(x, y, 1+z)$, respectively. For the sake of clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered phenyl ring is shown.

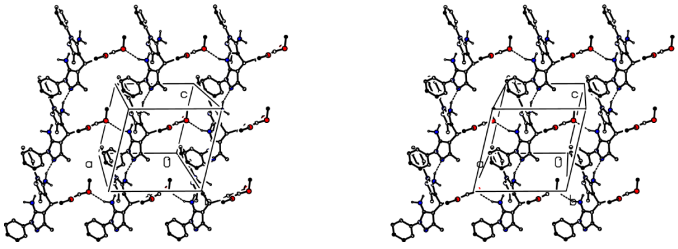


Figure 4
Stereoview of part of the crystal structure of compound (I), showing the formation of a (010) sheet by combination of the [100] and [001] chains. For the sake of clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered phenyl ring is shown.

interactions in the structure and, despite the presence of three independent aryl rings, there are neither X—H···π(arene) hydrogen bonds (X = C or N) nor aromatic π–π 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%; $C_{30}H_{32}N_6O_3$ requires C 68.7, H 6.1, N 16.0%.

Crystal data

$C_{30}H_{32}N_6O_3$
M_r = 524.62
Monoclinic, $P2_1/c$
a = 9.7540 (2) Å
b = 33.4646 (7) Å
c = 8.9010 (1) Å
β = 103.6020 (9)°
V = 2823.92 (9) Å^3
Z = 4
D_x = 1.234 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5973 reflections
θ = 2.8–27.5°
μ = 0.08 mm^{-1}
T = 120 (2) K
Lath, orange
0.15 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.977, T_{max} = 0.996
25 815 measured reflections
4968 independent reflections
3683 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 25.0°
$h = -11 \rightarrow 11$
$k = -39 \rightarrow 39$
$l = -10 \rightarrow 10$

Refinement

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

Table 1
Selected geometric parameters (Å, °).

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—C23*A*—C23*B*	−63.5 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N12—H12*A*···N22	0.93	2.28	3.194 (3)	167
N12—H12*B*···O34^{i}	0.95	2.37	3.255 (3)	154
N22—H22*A*···N14^{ii}	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 Å (aliphatic CH), and with U_{iso}(H) =

$1.2U_{eq}$(C), or $1.5U_{eq}$(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_{iso}(H) = $1.2U_{eq}$(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 *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JC thanks the Consejería de Educación y Ciencia (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JP and JQ thank COLCIENCIAS and the Universidad de Valle for financial support.

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supporting information

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$c = 8.9010$ (1) Å
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$V = 2823.92$ (9) Å^3
$Z = 4$
$F(000) = 1112$
$D_x = 1.234$ Mg m^{-3}
Melting point: 593 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5973 reflections
$\theta = 2.8$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 120$ K
Lath, orange
0.15 × 0.10 × 0.05 mm

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Nonius KappaCCD diffractometer
Radiation source: rotating anode
Graphite monochromator
φ scans, and ω scans with κ offsets
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3683 reflections with $I > 2\sigma(I)$
$R_{int} = 0.081$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.8°$
$h = -11 \rightarrow 11$
$k = -39 \rightarrow 39$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.144$
$S = 1.04$
4968 reflections
388 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 1.5741P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O33	0.03953 (16)	0.09322 (5)	0.5362 (2)	0.0423 (4)	

O34	0.04151 (17)	0.17261 (5)	0.5385 (2)	0.0441 (4)	
O35	0.24759 (18)	0.21453 (5)	0.4570 (2)	0.0491 (5)	
N12	0.71208 (19)	0.15462 (5)	0.3757 (2)	0.0325 (4)	
N13	0.66203 (18)	0.14985 (5)	0.0989 (2)	0.0294 (4)	
N14	0.5663 (2)	0.13217 (6)	−0.0230 (2)	0.0343 (5)	
N22	0.6063 (2)	0.11891 (5)	0.6615 (2)	0.0349 (5)	
N23	0.70756 (19)	0.05277 (6)	0.6710 (2)	0.0347 (5)	
N24	0.70871 (19)	0.01969 (6)	0.5780 (2)	0.0360 (5)	
C1	0.4606 (2)	0.08836 (6)	0.3166 (2)	0.0253 (5)	
C11	0.5289 (2)	0.11103 (6)	0.2071 (2)	0.0264 (5)	
C12	0.6408 (2)	0.13773 (6)	0.2382 (2)	0.0262 (5)	
C15	0.4885 (2)	0.10902 (7)	0.0452 (3)	0.0309 (5)	
C21	0.5644 (2)	0.06829 (6)	0.4476 (2)	0.0239 (5)	
C22	0.6207 (2)	0.08213 (6)	0.5949 (2)	0.0277 (5)	
C25	0.6227 (2)	0.02975 (6)	0.4442 (3)	0.0295 (5)	
C31	0.3494 (2)	0.11207 (6)	0.3750 (2)	0.0269 (5)	
C32	0.2484 (2)	0.09063 (7)	0.4297 (2)	0.0288 (5)	
C33	0.1475 (2)	0.11103 (7)	0.4867 (3)	0.0313 (5)	
C34	0.1481 (2)	0.15240 (7)	0.4919 (3)	0.0338 (5)	
C35	0.2520 (2)	0.17385 (7)	0.4420 (3)	0.0361 (6)	
C36	0.3510 (2)	0.15350 (6)	0.3804 (3)	0.0322 (5)	
C131	0.7540 (2)	0.17951 (7)	0.0627 (3)	0.0319 (5)	
C132	0.8928 (3)	0.18194 (8)	0.1436 (3)	0.0425 (6)	
C133	0.9790 (3)	0.21110 (9)	0.1029 (3)	0.0551 (8)	
C134	0.9294 (3)	0.23626 (8)	−0.0186 (3)	0.0564 (8)	
C135	0.7919 (3)	0.23328 (8)	−0.1006 (3)	0.0529 (7)	
C136	0.7026 (3)	0.20502 (7)	−0.0603 (3)	0.0412 (6)	
C151	0.3733 (3)	0.08398 (8)	−0.0526 (3)	0.0454 (6)	
C231	0.7982 (6)	0.04803 (13)	0.8170 (4)	0.0372 (19)	0.50
C232	0.8746 (7)	0.08097 (11)	0.8860 (5)	0.0348 (15)	0.50
C233	0.9671 (6)	0.07720 (11)	1.0301 (5)	0.057 (2)	0.50
C234	0.9833 (5)	0.04048 (12)	1.1053 (4)	0.091 (3)	0.50
C235	0.9069 (5)	0.00754 (10)	1.0363 (5)	0.085 (2)	0.50
C236	0.8144 (5)	0.01132 (11)	0.8921 (4)	0.0482 (14)	0.50
C23A	0.7905 (5)	0.06105 (18)	0.8283 (4)	0.044 (2)	0.50
C23B	0.8921 (5)	0.09100 (16)	0.8521 (4)	0.0352 (17)	0.50
C23C	0.9711 (4)	0.09902 (14)	1.0005 (5)	0.0516 (16)	0.50
C23D	0.9485 (4)	0.07710 (19)	1.1251 (4)	0.086 (3)	0.50
C23E	0.8469 (5)	0.0471 (2)	1.1013 (4)	0.122 (4)	0.50
C23F	0.7679 (5)	0.03912 (17)	0.9529 (5)	0.096 (3)	0.50
C251	0.5960 (3)	0.00183 (7)	0.3102 (3)	0.0405 (6)	
C331	0.0416 (3)	0.05079 (7)	0.5491 (4)	0.0530 (8)	
C341	0.0653 (3)	0.17745 (9)	0.7018 (3)	0.0571 (8)	
C351	0.3606 (3)	0.23690 (8)	0.4213 (4)	0.0611 (9)	
H12A	0.6962	0.1435	0.4657	0.039*	
H12B	0.8110	0.1585	0.3900	0.039*	
H22A	0.6202	0.1193	0.7720	0.042*	
H22B	0.5206	0.1309	0.6112	0.042*	

H1	0.4077	0.0660	0.2539	0.030*	
H32	0.2487	0.0622	0.4279	0.035*	
H36	0.4193	0.1680	0.3423	0.039*	
H132	0.9290	0.1640	0.2259	0.051*	
H133	1.0739	0.2136	0.1604	0.066*	
H134	0.9899	0.2558	−0.0463	0.068*	
H135	0.7575	0.2507	−0.1854	0.064*	
H136	0.6072	0.2032	−0.1166	0.049*	
H15A	0.3662	0.0898	−0.1621	0.068*	
H15B	0.2834	0.0902	−0.0267	0.068*	
H15C	0.3953	0.0556	−0.0328	0.068*	
H232	0.8636	0.1061	0.8346	0.042*	0.50
H233	1.0193	0.0997	1.0773	0.069*	0.50
H234	1.0465	0.0379	1.2038	0.109*	0.50
H235	0.9179	−0.0175	1.0876	0.102*	0.50
H236	0.7622	−0.0112	0.8449	0.058*	0.50
H23B	0.9075	0.1060	0.7669	0.042*	0.50
H23C	1.0405	0.1195	1.0168	0.062*	0.50
H23D	1.0024	0.0826	1.2265	0.104*	0.50
H23E	0.8315	0.0322	1.1864	0.147*	0.50
H23F	0.6985	0.0186	0.9366	0.115*	0.50
H25A	0.6415	0.0121	0.2309	0.061*	
H25B	0.4942	−0.0005	0.2670	0.061*	
H25C	0.6348	−0.0245	0.3445	0.061*	
H33A	0.0439	0.0389	0.4491	0.080*	
H33B	−0.0432	0.0418	0.5803	0.080*	
H33C	0.1256	0.0425	0.6269	0.080*	
H34A	0.0844	0.1513	0.7522	0.086*	
H34B	−0.0186	0.1892	0.7269	0.086*	
H34C	0.1464	0.1951	0.7385	0.086*	
H35A	0.4509	0.2261	0.4797	0.092*	
H35B	0.3525	0.2650	0.4493	0.092*	
H35C	0.3559	0.2349	0.3104	0.092*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O33	0.0339 (9)	0.0427 (10)	0.0588 (11)	−0.0050 (7)	0.0281 (8)	−0.0045 (8)
O34	0.0378 (10)	0.0453 (10)	0.0562 (12)	0.0108 (8)	0.0250 (8)	−0.0010 (8)
O35	0.0523 (11)	0.0278 (9)	0.0767 (13)	0.0074 (7)	0.0342 (10)	0.0052 (9)
N12	0.0359 (11)	0.0383 (11)	0.0250 (10)	−0.0092 (8)	0.0105 (8)	−0.0009 (8)
N13	0.0324 (10)	0.0342 (10)	0.0242 (10)	−0.0066 (8)	0.0120 (8)	−0.0007 (8)
N14	0.0373 (11)	0.0433 (12)	0.0241 (10)	−0.0075 (9)	0.0106 (8)	−0.0014 (8)
N22	0.0467 (12)	0.0354 (11)	0.0246 (10)	−0.0078 (9)	0.0123 (9)	−0.0042 (8)
N23	0.0304 (10)	0.0406 (12)	0.0310 (11)	−0.0073 (8)	0.0031 (8)	0.0094 (9)
N24	0.0275 (10)	0.0328 (11)	0.0491 (13)	−0.0001 (8)	0.0120 (9)	0.0065 (9)
C1	0.0261 (11)	0.0283 (11)	0.0235 (11)	−0.0027 (9)	0.0099 (9)	−0.0015 (9)
C11	0.0277 (11)	0.0287 (11)	0.0250 (11)	−0.0018 (9)	0.0106 (9)	−0.0005 (9)

C12	0.0285 (11)	0.0301 (12)	0.0226 (11)	0.0004 (9)	0.0111 (9)	0.0000 (9)
C15	0.0325 (12)	0.0363 (13)	0.0262 (12)	−0.0039 (9)	0.0114 (10)	−0.0022 (10)
C21	0.0237 (10)	0.0258 (11)	0.0249 (11)	−0.0023 (8)	0.0108 (9)	−0.0003 (9)
C22	0.0304 (11)	0.0289 (12)	0.0258 (12)	−0.0058 (9)	0.0107 (9)	0.0027 (9)
C25	0.0249 (11)	0.0275 (12)	0.0402 (13)	−0.0024 (9)	0.0161 (10)	0.0009 (10)
C31	0.0254 (11)	0.0321 (12)	0.0244 (11)	0.0014 (9)	0.0083 (9)	0.0029 (9)
C32	0.0272 (11)	0.0301 (12)	0.0311 (12)	−0.0022 (9)	0.0107 (9)	−0.0023 (9)
C33	0.0244 (11)	0.0386 (13)	0.0334 (13)	−0.0011 (9)	0.0120 (10)	0.0018 (10)
C34	0.0295 (12)	0.0362 (13)	0.0397 (14)	0.0086 (10)	0.0165 (10)	0.0023 (11)
C35	0.0361 (13)	0.0280 (12)	0.0475 (15)	0.0053 (10)	0.0165 (11)	0.0056 (11)
C36	0.0312 (12)	0.0307 (12)	0.0387 (13)	0.0014 (9)	0.0165 (10)	0.0070 (10)
C131	0.0402 (13)	0.0294 (12)	0.0319 (13)	−0.0042 (10)	0.0203 (11)	−0.0027 (10)
C132	0.0430 (15)	0.0496 (15)	0.0382 (14)	−0.0127 (12)	0.0159 (12)	0.0012 (12)
C133	0.0533 (17)	0.0670 (19)	0.0497 (17)	−0.0277 (14)	0.0213 (14)	−0.0066 (15)
C134	0.083 (2)	0.0428 (16)	0.0548 (18)	−0.0276 (15)	0.0383 (17)	−0.0081 (14)
C135	0.084 (2)	0.0310 (14)	0.0529 (17)	−0.0026 (14)	0.0341 (16)	0.0074 (12)
C136	0.0510 (15)	0.0329 (13)	0.0456 (15)	0.0042 (11)	0.0230 (12)	0.0075 (11)
C151	0.0459 (15)	0.0613 (17)	0.0289 (13)	−0.0173 (13)	0.0087 (11)	−0.0030 (12)
C231	0.036 (4)	0.040 (4)	0.031 (4)	−0.010 (3)	−0.001 (3)	0.005 (2)
C232	0.033 (3)	0.040 (4)	0.032 (3)	−0.012 (3)	0.010 (3)	0.000 (3)
C233	0.067 (4)	0.044 (4)	0.044 (4)	−0.021 (3)	−0.021 (3)	0.008 (3)
C234	0.110 (7)	0.070 (5)	0.058 (4)	−0.021 (4)	−0.047 (4)	0.013 (4)
C235	0.107 (6)	0.058 (4)	0.060 (4)	−0.027 (4)	−0.041 (4)	0.022 (3)
C236	0.059 (4)	0.036 (3)	0.037 (3)	−0.011 (3)	−0.014 (3)	0.006 (2)
C23A	0.024 (4)	0.073 (5)	0.034 (4)	−0.004 (3)	0.005 (3)	0.023 (3)
C23B	0.026 (3)	0.046 (4)	0.035 (4)	−0.001 (3)	0.011 (3)	−0.001 (3)
C23C	0.039 (3)	0.072 (5)	0.042 (4)	0.005 (3)	0.006 (3)	0.000 (4)
C23D	0.044 (4)	0.174 (9)	0.038 (4)	0.003 (5)	0.001 (3)	0.021 (5)
C23E	0.066 (5)	0.242 (12)	0.047 (4)	−0.055 (6)	−0.009 (4)	0.075 (6)
C23F	0.043 (4)	0.171 (9)	0.061 (5)	−0.042 (5)	−0.014 (3)	0.066 (5)
C251	0.0435 (14)	0.0307 (13)	0.0548 (16)	0.0000 (10)	0.0265 (12)	−0.0058 (11)
C331	0.0547 (17)	0.0386 (15)	0.080 (2)	−0.0166 (12)	0.0436 (16)	−0.0132 (14)
C341	0.069 (2)	0.0523 (17)	0.0603 (19)	0.0059 (14)	0.0357 (16)	−0.0078 (14)
C351	0.0636 (19)	0.0286 (14)	0.103 (3)	−0.0032 (12)	0.0444 (18)	0.0042 (15)

Geometric parameters (Å, º)

O33—C33	1.370 (2)	C133—H133	0.95
O33—C331	1.424 (3)	C134—C135	1.371 (4)
O34—C34	1.383 (3)	C134—H134	0.95
O34—C341	1.426 (3)	C135—C136	1.388 (4)
O35—C35	1.370 (3)	C135—H135	0.95
O35—C351	1.428 (3)	C136—H136	0.95
C11—C12	1.387 (3)	C151—H15A	0.98
C12—N13	1.366 (3)	C151—H15B	0.98
N13—N14	1.387 (3)	C151—H15C	0.98
N14—C15	1.327 (3)	C231—C232	1.39
C15—C11	1.403 (3)	C231—C236	1.39

C12—N12	1.378 (3)	C232—C233	1.39
C1—C11	1.508 (3)	C232—H232	0.95
C1—C21	1.510 (3)	C233—C234	1.39
C1—C31	1.530 (3)	C233—H233	0.95
C21—C22	1.377 (3)	C234—C235	1.39
C22—N23	1.368 (3)	C234—H234	0.95
N23—N24	1.384 (3)	C235—C236	1.39
N24—C25	1.329 (3)	C235—H235	0.95
C25—C21	1.412 (3)	C236—H236	0.95
C22—N22	1.388 (3)	C23A—C23B	1.39
N12—H12A	0.9293	C23A—C23F	1.39
N12—H12B	0.9514	C23B—C23C	1.39
N13—C131	1.425 (3)	C23B—H23B	0.95
N22—H22A	0.9611	C23C—C23D	1.39
N22—H22B	0.9399	C23C—H23C	0.95
N23—C231	1.398 (3)	C23D—C23E	1.39
N23—C23A	1.469 (4)	C23D—H23D	0.95
C1—H1	1.00	C23E—C23F	1.39
C15—C151	1.504 (3)	C23E—H23E	0.95
C25—C251	1.489 (3)	C23F—H23F	0.95
C31—C36	1.387 (3)	C251—H25A	0.98
C31—C32	1.396 (3)	C251—H25B	0.98
C32—C33	1.388 (3)	C251—H25C	0.98
C32—H32	0.95	C331—H33A	0.98
C33—C34	1.385 (3)	C331—H33B	0.98
C34—C35	1.397 (3)	C331—H33C	0.98
C35—C36	1.395 (3)	C341—H34A	0.98
C36—H36	0.95	C341—H34B	0.98
C131—C132	1.378 (3)	C341—H34C	0.98
C131—C136	1.386 (3)	C351—H35A	0.98
C132—C133	1.391 (3)	C351—H35B	0.98
C132—H132	0.95	C351—H35C	0.98
C133—C134	1.366 (4)		

C33—O33—C331	117.52 (17)	C134—C135—C136	120.4 (3)
C34—O34—C341	114.03 (19)	C134—C135—H135	119.8
C35—O35—C351	117.12 (18)	C136—C135—H135	119.8
C12—N12—H12A	116.7	C131—C136—C135	119.4 (3)
C12—N12—H12B	117.2	C131—C136—H136	120.3
H12A—N12—H12B	108.0	C135—C136—H136	120.3
C12—N13—N14	111.46 (16)	C15—C151—H15A	109.5
C12—N13—C131	130.57 (18)	C15—C151—H15B	109.5
N14—N13—C131	117.64 (17)	H15A—C151—H15B	109.5
C15—N14—N13	104.07 (17)	C15—C151—H15C	109.5
C22—N22—H22A	116.4	H15A—C151—H15C	109.5
C22—N22—H22B	110.0	H15B—C151—H15C	109.5
H22A—N22—H22B	112.2	C232—C231—C236	120.0
C22—N23—N24	111.67 (18)	C232—C231—N23	118.5 (3)

C22—N23—C231	136.4 (3)	C236—C231—N23	121.5 (3)
N24—N23—C231	111.9 (3)	C233—C232—C231	120.0
C22—N23—C23A	118.3 (3)	C233—C232—H232	120.0
N24—N23—C23A	129.9 (3)	C231—C232—H232	120.0
C25—N24—N23	103.97 (17)	C232—C233—C234	120.0
C11—C1—C21	113.88 (16)	C232—C233—H233	120.0
C11—C1—C31	114.53 (17)	C234—C233—H233	120.0
C21—C1—C31	111.59 (16)	C235—C234—C233	120.0
C11—C1—H1	105.3	C235—C234—H234	120.0
C21—C1—H1	105.3	C233—C234—H234	120.0
C31—C1—H1	105.3	C234—C235—C236	120.0
C12—C11—C15	104.73 (18)	C234—C235—H235	120.0
C12—C11—C1	129.87 (19)	C236—C235—H235	120.0
C15—C11—C1	125.40 (19)	C235—C236—C231	120.0
N13—C12—N12	122.13 (18)	C235—C236—H236	120.0
N13—C12—C11	106.84 (18)	C231—C236—H236	120.0
N12—C12—C11	130.57 (19)	C23B—C23A—C23F	120.0
N14—C15—C11	112.89 (19)	C23B—C23A—N23	119.6 (3)
N14—C15—C151	119.31 (19)	C23F—C23A—N23	120.4 (3)
C11—C15—C151	127.79 (19)	C23C—C23B—C23A	120.0
C22—C21—C25	104.81 (19)	C23C—C23B—H23B	120.0
C22—C21—C1	129.08 (19)	C23A—C23B—H23B	120.0
C25—C21—C1	126.09 (19)	C23D—C23C—C23B	120.0
N23—C22—C21	106.96 (19)	C23D—C23C—H23C	120.0
N23—C22—N22	122.6 (2)	C23B—C23C—H23C	120.0
C21—C22—N22	130.3 (2)	C23C—C23D—C23E	120.0
N24—C25—C21	112.59 (19)	C23C—C23D—H23D	120.0
N24—C25—C251	120.9 (2)	C23E—C23D—H23D	120.0
C21—C25—C251	126.5 (2)	C23F—C23E—C23D	120.0
C36—C31—C32	120.30 (19)	C23F—C23E—H23E	120.0
C36—C31—C1	121.82 (18)	C23D—C23E—H23E	120.0
C32—C31—C1	117.83 (18)	C23E—C23F—C23A	120.0
C33—C32—C31	119.6 (2)	C23E—C23F—H23F	120.0
C33—C32—H32	120.2	C23A—C23F—H23F	120.0
C31—C32—H32	120.2	C25—C251—H25A	109.5
O33—C33—C32	124.6 (2)	C25—C251—H25B	109.5
O34—C34—C33	120.1 (2)	H25A—C251—H25B	109.5
O35—C35—C34	116.0 (2)	C25—C251—H25C	109.5
O33—C33—C34	114.9 (2)	H25A—C251—H25C	109.5
O34—C34—C35	119.8 (2)	H25B—C251—H25C	109.5
O35—C35—C36	124.3 (2)	O33—C331—H33A	109.5
C34—C33—C32	120.39 (19)	O33—C331—H33B	109.5
C33—C34—C35	120.04 (19)	H33A—C331—H33B	109.5
C36—C35—C34	119.7 (2)	O33—C331—H33C	109.5
C31—C36—C35	119.92 (19)	H33A—C331—H33C	109.5
C31—C36—H36	120.0	H33B—C331—H33C	109.5
C35—C36—H36	120.0	O34—C341—H34A	109.5
C132—C131—C136	120.3 (2)	O34—C341—H34B	109.5

C132—C131—N13	121.1 (2)	H34A—C341—H34B	109.5
C136—C131—N13	118.6 (2)	O34—C341—H34C	109.5
C131—C132—C133	119.0 (3)	H34A—C341—H34C	109.5
C131—C132—H132	120.5	H34B—C341—H34C	109.5
C133—C132—H132	120.5	O35—C351—H35A	109.5
C134—C133—C132	121.0 (3)	O35—C351—H35B	109.5
C134—C133—H133	119.5	H35A—C351—H35B	109.5
C132—C133—H133	119.5	O35—C351—H35C	109.5
C133—C134—C135	119.8 (2)	H35A—C351—H35C	109.5
C133—C134—H134	120.1	H35B—C351—H35C	109.5
C135—C134—H134	120.1		

C31—C1—C11—C12	83.3 (3)	C331—O33—C33—C34	−173.5 (2)
C331—O33—C33—C32	8.6 (3)	C31—C32—C33—O33	176.7 (2)
C341—O34—C34—C33	85.8 (3)	C31—C32—C33—C34	−1.1 (3)
C22—N23—C231—C232	−35.9 (5)	C341—O34—C34—C35	−97.8 (3)
C31—C1—C21—C22	−37.3 (3)	O33—C33—C34—O34	−2.6 (3)
C351—O35—C35—C36	−6.5 (4)	C32—C33—C34—O34	175.4 (2)
C12—N13—C131—C132	45.9 (3)	O33—C33—C34—C35	−179.0 (2)
C22—N23—C23A—C23B	−63.5 (4)	C32—C33—C34—C35	−1.0 (4)
C12—N13—N14—C15	−0.6 (2)	C351—O35—C35—C34	173.9 (2)
C131—N13—N14—C15	−174.70 (19)	O34—C34—C35—O35	6.0 (3)
C22—N23—N24—C25	0.7 (2)	C33—C34—C35—O35	−177.5 (2)
C231—N23—N24—C25	−177.6 (3)	O34—C34—C35—C36	−173.5 (2)
C23A—N23—N24—C25	−174.6 (3)	C33—C34—C35—C36	2.9 (4)
C21—C1—C11—C12	−46.8 (3)	C32—C31—C36—C35	0.6 (3)
C21—C1—C11—C15	133.5 (2)	C1—C31—C36—C35	−176.7 (2)
C31—C1—C11—C15	−96.4 (2)	O35—C35—C36—C31	177.8 (2)
N14—N13—C12—N12	−172.41 (18)	C34—C35—C36—C31	−2.7 (4)
C131—N13—C12—N12	0.7 (3)	N14—N13—C131—C132	−141.4 (2)
N14—N13—C12—C11	0.6 (2)	C12—N13—C131—C136	−136.7 (2)
C131—N13—C12—C11	173.7 (2)	N14—N13—C131—C136	36.1 (3)
C15—C11—C12—N13	−0.3 (2)	C136—C131—C132—C133	1.9 (4)
C1—C11—C12—N13	179.9 (2)	N13—C131—C132—C133	179.3 (2)
C15—C11—C12—N12	171.9 (2)	C131—C132—C133—C134	−2.2 (4)
C1—C11—C12—N12	−7.9 (4)	C132—C133—C134—C135	1.1 (4)
N13—N14—C15—C11	0.4 (2)	C133—C134—C135—C136	0.4 (4)
N13—N14—C15—C151	−178.7 (2)	C132—C131—C136—C135	−0.5 (4)
C12—C11—C15—N14	0.0 (3)	N13—C131—C136—C135	−178.0 (2)
C1—C11—C15—N14	179.78 (19)	C134—C135—C136—C131	−0.7 (4)
C12—C11—C15—C151	178.9 (2)	N24—N23—C231—C232	141.9 (3)
C1—C11—C15—C151	−1.3 (4)	C23A—N23—C231—C232	−30.6 (11)
C11—C1—C21—C22	94.3 (2)	C22—N23—C231—C236	145.0 (3)
C11—C1—C21—C25	−87.3 (2)	N24—N23—C231—C236	−37.2 (5)
C31—C1—C21—C25	141.10 (19)	C23A—N23—C231—C236	150.2 (15)
N24—N23—C22—C21	−0.7 (2)	C236—C231—C232—C233	0.0
C231—N23—C22—C21	177.1 (4)	N23—C231—C232—C233	−179.2 (5)
C23A—N23—C22—C21	175.3 (3)	C231—C232—C233—C234	0.0

N24—N23—C22—N22	−177.18 (17)	C232—C233—C234—C235	0.0
C231—N23—C22—N22	0.6 (5)	C233—C234—C235—C236	0.0
C23A—N23—C22—N22	−1.2 (3)	C234—C235—C236—C231	0.0
C25—C21—C22—N23	0.3 (2)	C232—C231—C236—C235	0.0
C1—C21—C22—N23	178.96 (18)	N23—C231—C236—C235	179.1 (5)
C25—C21—C22—N22	176.5 (2)	N24—N23—C23A—C23B	111.6 (3)
C1—C21—C22—N22	−4.9 (4)	C231—N23—C23A—C23B	120.6 (14)
N23—N24—C25—C21	−0.5 (2)	C22—N23—C23A—C23F	116.5 (3)
N23—N24—C25—C251	179.36 (18)	N24—N23—C23A—C23F	−68.4 (5)
C22—C21—C25—N24	0.1 (2)	C231—N23—C23A—C23F	−59.4 (11)
C1—C21—C25—N24	−178.55 (17)	C23F—C23A—C23B—C23C	0.0
C22—C21—C25—C251	−179.7 (2)	N23—C23A—C23B—C23C	180.0 (5)
C1—C21—C25—C251	1.6 (3)	C23A—C23B—C23C—C23D	0.0
C11—C1—C31—C36	−24.8 (3)	C23B—C23C—C23D—C23E	0.0
C21—C1—C31—C36	106.5 (2)	C23C—C23D—C23E—C23F	0.0
C11—C1—C31—C32	157.90 (19)	C23D—C23E—C23F—C23A	0.0
C21—C1—C31—C32	−70.9 (2)	C23B—C23A—C23F—C23E	0.0
C36—C31—C32—C33	1.3 (3)	N23—C23A—C23F—C23E	180.0 (5)
C1—C31—C32—C33	178.68 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12*A*···N22	0.93	2.28	3.194 (3)	167
N12—H12*B*···O34^{i}	0.95	2.37	3.255 (3)	154
N22—H22*A*···N14^{ii}	0.96	2.06	2.958 (3)	155

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