Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

7-Amino-5-methyl-2-phenyl-6-(phenyldiazenyl)pyrazolo[1,5-*a*]pyrimidine crystallizes with Z' = 2: pseudo-symmetry and the formation of complex sheets built from N—H···N and C—H···π(arene) hydrogen bonds

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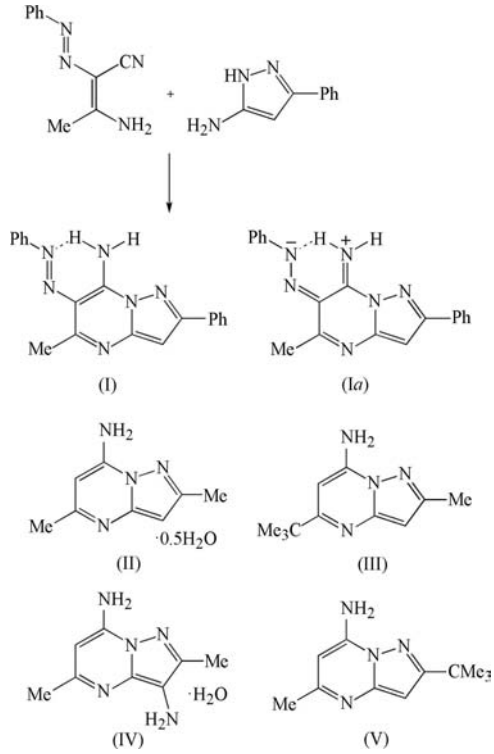
Received 28 January 2010
Accepted 28 January 2010
Online 24 February 2010

The title compound, $C_{19}H_{16}N_6$, crystallizes with Z' = 2 in the space group $P2_1/n$. The two molecules in the selected asymmetric unit are approximate mirror images of one another; most corresponding pairs of atoms are related by an approximate half-cell translation along [100]. Each molecule contains an intramolecular N—H···N hydrogen bond and the molecules are linked into complex sheets by a combination of two intermolecular N—H···N and four C—H···π(arene) hydrogen bonds. Comparisons are made with some other 7-aminopyrazolo[1,5-*a*]pyrimidines.

Comment

Fused pyrazole derivatives are of potential value in a wide range of drug, pesticide and new materials applications (Elguero, 1984, 1996) and, associated with a synthetic study of these systems, we report here the structure of the title compound, (I) (Fig. 1). This compound was prepared rapidly and in high yield by means of a cyclization reaction between 5-amino-3-phenyl-1*H*-pyrazole and 3-amino-2-phenyldiazenyl-2-butenenitrile (3-amino-3-methyl-2-phenyldiazenylacrylonitrile), mediated by microwave radiation under solvent-free (green) conditions (see scheme). Compound (I) shows unexpected crystallization behaviour and an interesting supramolecular structure.

Compound (I) crystallizes with Z' = 2 in the space group $P2_1/n$; it is convenient to describe the independent molecules containing atoms N11 (Fig. 1*a*) and N21 (Fig. 1*b*) as molecules of types 1 and 2, respectively. The presence of two independent molecules necessarily introduces some flexibility into the choice of the asymmetric unit, but for (I) it is possible to specify a compact asymmetric unit in which the two independent molecules are linked by two C—H···π(arene) hydrogen bonds (Table 2 and Fig. 2). With the exception of the *ortho* and *meta* positions of the terminal phenyl rings, the coordinates of corresponding pairs of atoms in the two molecules in the selected asymmetric unit are approximately related by the transformation ($\frac{1}{2}$ + x, y, z). In each of the two molecules, the skeletons between atoms C*n*21 and C*n*61, where n = 1 or 2 (Fig. 1), are close to planarity, as indicated by the relevant torsion angles (Table 1). However, while the torsion angles describing the orientations of the phenyl rings have similar magnitudes in the two independent molecules, the corresponding pairs of values have opposite signs, indicating that the two molecules in the selected asymmetric unit are approximate, but not exact, mirror images of one another. The combination of the approximate translational relationship between these molecules and their approximate conformational enantiomerism precludes the possibility of any additional symmetry. The differences in the hydrogen-bonding behaviour of the two molecules, discussed below, further confirms the absence of any additional crystallographic symmetry.



The bond distances within the pyrazolo[1,5-*a*]pyrimidine unit of compound (I) are very similar in the two independent molecules (Table 1), and they are consistent with a more marked degree of bond fixation with alternating single and double bonds between atoms N*n*1 and N*n*7 (n = 1 or 2) (see scheme). This geometry may be contrasted with that found in the simpler analogues (II) (Portilla, Quiroga, Cobo *et al.*, 2006), (III) and (IV) (Portilla, Quiroga, de la Torre *et al.*,

 doi:10.1107/S0108270110003549

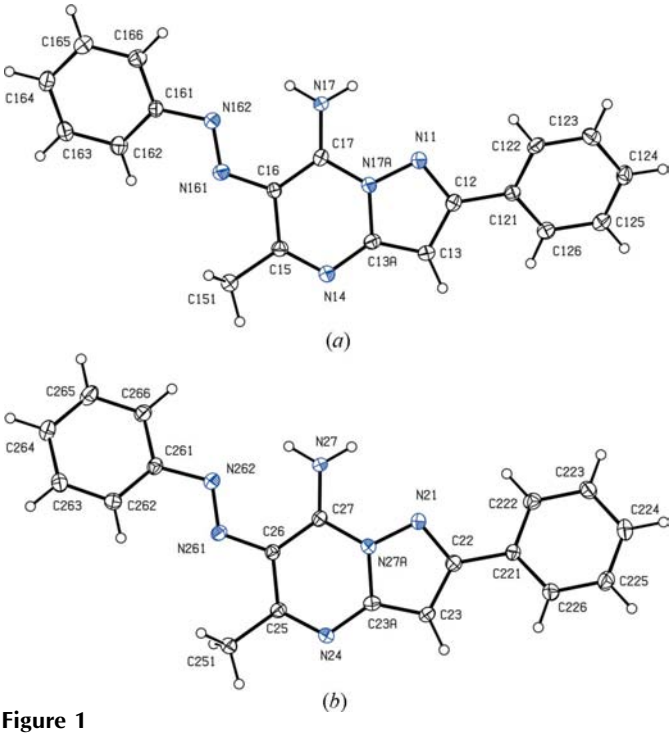


Figure 1
The independent molecular components of compound (I), showing the atom-labelling scheme for (*a*) the type 1 molecule and (*b*) the type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level.

2006), and (V) (Portilla *et al.*, 2007), which exhibit naphthalene-type delocalization. In addition, the exocyclic C—N bonds C*n*7—N*n*7 (*n* = 1 or 2) are very much shorter in compound (I) than in analogues (II)–(V), where the corresponding distances range from 1.330 (2) Å for one of the molecules in (III) to 1.3705 (19) Å in (V). The short exocyclic C—N distances in (I) may be associated both with the more strongly localized electronic structure of the pyrazolo[1,5-*a*]-pyrimidine unit in (I), and with possible delocalization into the phenyldiazenyl substituent: the distances N*n*61—N*n*62 (*n* = 1 or 2) are long for their type [mean value (Allen *et al.*, 1987) 1.222 Å, upper quartile value 1.227 Å], while the bonds C*n*6—N*n*61 are much shorter than the bonds N*n*62—C*n*61, suggesting some contribution to the overall electronic structure of (I) from polarized form (I*a*). On this basis, the short intramolecular N—H···N hydrogen bonds (Table 2) can be regarded as charge-assisted hydrogen bonds (Gilli *et al.*, 1994).

The molecules of compound (I) are linked into complex sheets by a combination of two N—H···N hydrogen bonds and four C—H···π(arene) hydrogen bonds (Table 2). The formation of the sheet can readily be analysed in terms of two ladder-like substructures, each of them one-dimensional.

In one of the substructures, formation of the ladder-type structure depends upon the combination of the intermolecular N—H···N hydrogen bonds with the two C—H···π(arene) hydrogen bonds within the asymmetric unit. Type 1 molecules which are related by the *n*-glide plane at $y = 0.25$ are linked by an N—H···N hydrogen bond to form a $C(6)$ (Bernstein *et al.*, 1995) chain running parallel to the [101] direction, and an entirely similar chain is formed by the type 2 molecules.

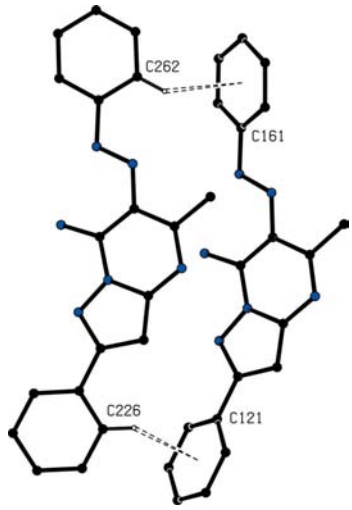


Figure 2
The two independent molecules in the selected asymmetric unit of compound (I), showing the two C—H···π(arene) hydrogen bonds within the asymmetric unit. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

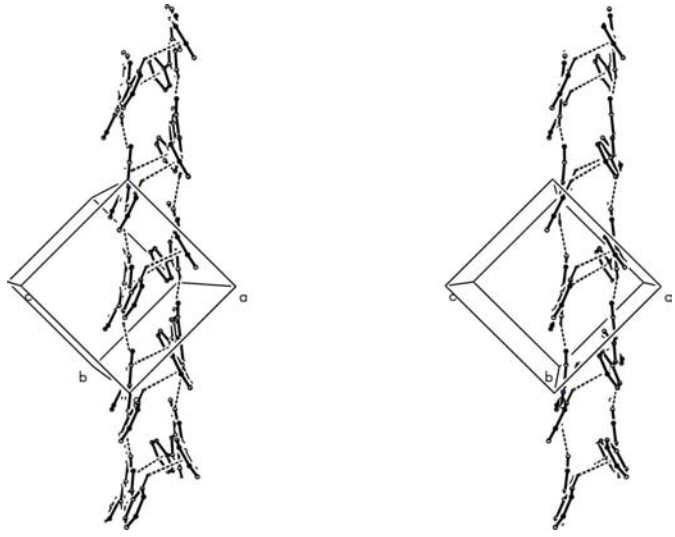


Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded molecular ladder along [101] built from N—H···N and C—H···π(arene) hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

Within each pair of molecules, one each of types 1 and 2, at any given symmetry position, the molecules are linked by two C—H···π(arene) hydrogen bonds. Hence, the substructure parallel to [101] takes the form of a molecular ladder (Fig. 3), in which the uprights are formed by the $C(6)$ chains of N—H···N hydrogen bonds and the treads are formed by the paired C—H···π(arene) hydrogen bonds.

The second substructure is built solely from the four C—H···π(arene) hydrogen bonds, with the type 2 molecule acting as a fourfold donor of hydrogen bonds and the type 1 molecule as a fourfold acceptor (Table 2). This difference in donor and acceptor behaviour between the two independent molecules, which is evident only for the C—H···π(arene)

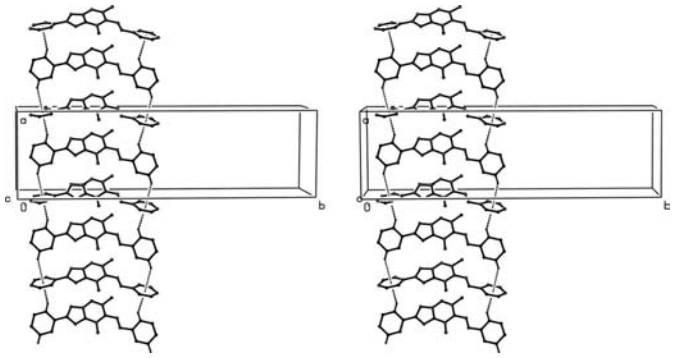


Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded molecular ladder along [100] built from C—H···π(arene) hydrogen bonds only. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

hydrogen bonds, not for the N—H···N hydrogen bonds, is a further indication of the absence of any additional crystallographic symmetry. Each of the aryl rings in the type 1 molecule acts as a double acceptor, with one donor atom bonding to each face of each ring, with H···*Cg*···H angles of 173 and 176° at the centroids of rings C121–C126 and C161–C166, respectively. The type 2 molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* C226 and C262, to the type 1 molecule at (*x*, *y*, *z*), and *via* C223 and C265 to the type 1 molecule at (−1 + *x*, *y*, *z*), so forming by translation a molecular ladder running parallel to the [100] direction (Fig. 4); here the uprights of the ladder are provided by the hydrogen bonds, and the treads are provided by the molecules themselves. The combination of the molecular ladders along [100] and [101] generates a sheet of considerable complexity, which lies parallel to (010).

It is of interest briefly to compare the hydrogen bonding, and hence the supramolecular aggregation, in compound (I) with that in the analogous 7-aminopyrazolo[1,5-*a*]pyrimidines (II)–(V) (see scheme), none of which contain any phenyl groups. Whereas the intermolecular N—H···N hydrogen bonds in compound (I) generate two independent *C*(6) chains, in each of compounds (II)–(V) pairs of molecules are linked by pairs of N—H···N hydrogen bonds to form dimeric units containing $R_2^2(10)$ motifs. In compounds (II) (Portilla, Quiroga, Cobo *et al.*, 2006), (IV) (Portilla, Quiroga, de la Torre *et al.*, 2006) and (V) (Portilla *et al.*, 2007), the dimers are formed from pairs of molecules related, respectively, by a twofold rotation in the space group *C*2, by inversion in the space group $P2_1/c$, and again by a twofold rotation, this time in the space group $P4_12_12$ (or $P4_32_12$). In compound (III), which crystallizes with $Z' = 2$ in the space group $P\overline{1}$ (Portilla, Quiroga, de la Torre *et al.*, 2006), the two molecules in the asymmetric unit are linked by two independent N—H···N hydrogen bonds to form an $R_2^2(10)$ dimer having no crystallographic symmetry. Further hydrogen bonds, of N—H···O and O—H···N types, link the molecular components in compounds (II) and (IV) into three-dimensional framework structures, while N—H···N hydrogen bonds alone suffice to form a three-dimensional framework in compound (V). In compound (III), four independent N—H···N hydrogen bonds link the molecules into a ribbon containing three types of hydrogen-bonded ring, one of $R_2^2(1)$ type and two of $R_4^4(14)$ type. Thus, no two compounds in this rather closely related series (I)–(V) exhibit similar crystallization characteristics, in terms of the combination of Z' value and space group, and no two adopt the same hydrogen-bonded supramolecular structure.

Experimental

Equimolar quantities (1 mmol of each component) of 5-amino-3-phenyl-1*H*-pyrazole and 3-amino-2-phenyldiazenyl-2-butenenitrile were intimately mixed, and the mixture was placed in an open Pyrex-glass flask, in the absence of solvent, and irradiated in a domestic microwave oven for 5 min at 800 W. The resulting solid material was extracted with ethanol. After removal of the solvent, the product, (I), was recrystallized from dimethylformamide to give orange crystals suitable for single-crystal X-ray diffraction (yield 85%, m.p. 501–502 K). NMR (DMSO-d_6): δ(H) 2.75 (*s*, 3H, CH_3), 6.90 (*s*, 1H, 3-H), 7.40 (*t*, 1H, 64-H), 7.43 (*t*, 1H, 24-H), 7.48 (*t*, 2H, 63-H), 7.52 (*t*, 2H, 23-H), 8.05 (*d*, 2H, 62-H), 8.07 (*d*, 2H, 22-H), 8.98, 10.25 (2*s*, 2H, NH_2); δ(C) 22.2 (CH_3), 93.8 (C3), 117.8 (C6), 121.9 (C62), 126.9 (C22), 129.1 (C23), 129.5 (C24), 129.6 (C63), 129.7 (C64), 133.0 (C21) 140.0 (C7), 149.0 (C3a), 153.2 (C61), 157.2 (C2), 161.5 (C5). MS (70 eV) *m*/*z* (%): 328 (100, M^+), 313 (23), 77 (19).

Crystal data

$C_{19}H_{16}N_6$
M_r = 328.38
Monoclinic, $P2_1/n$
a = 9.6342 (13) Å
b = 33.216 (5) Å
c = 9.747 (3) Å
β = 90.237 (18)°
V = 3119.1 (11) Å^3
Z = 8
Mo *K*α radiation
μ = 0.09 mm^{-1}
T = 120 K
0.42 × 0.35 × 0.27 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.963, T_{max} = 0.976
35111 measured reflections
5790 independent reflections
3135 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.342 (3)	N21—C22	1.328 (3)
C12—C13	1.398 (4)	C22—C23	1.399 (4)
C13—C13*A*	1.357 (4)	C23—C23*A*	1.365 (4)
C13*A*—N14	1.359 (3)	C23*A*—N24	1.358 (3)
N14—C15	1.308 (3)	N24—C25	1.313 (3)
C15—C16	1.430 (4)	C25—C26	1.417 (4)
C16—C17	1.390 (4)	C26—C27	1.399 (4)
C17—N17*A*	1.356 (3)	C27—N27*A*	1.364 (3)
N17*A*—N11	1.363 (3)	N27*A*—N21	1.357 (3)
C13*A*—N17*A*	1.388 (3)	C23*A*—N27*A*	1.384 (3)
C17—N17	1.314 (3)	C27—N27	1.311 (3)
C16—N161	1.369 (3)	C26—N261	1.380 (3)
N161—N162	1.277 (3)	N261—N262	1.270 (3)
N162—C161	1.420 (3)	N262—C261	1.425 (3)
N11—C12—C121—C122	24.1 (4)	N21—C22—C221—C222	−20.3 (4)
C15—C16—N161—N162	−179.1 (2)	C25—C26—N261—N262	−177.1 (2)
C16—N161—N162—C161	175.2 (2)	C26—N261—N262—C261	179.0 (2)
N161—N162—C161—C162	−20.6 (4)	N261—N262—C261—C262	18.9 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N17—H17A···N14^{i}	0.88	2.29	2.972 (3)	134
N17—H17B···N162	0.88	2.08	2.691 (3)	125
N27—H27A···N24^{i}	0.88	2.30	2.953 (3)	131
N27—H27B···N262	0.88	2.05	2.656 (3)	125
C223—H223···$Cg1^{ii}$	0.95	2.95	3.701 (3)	137
C226—H226···$Cg1$	0.95	2.84	3.537 (3)	132
C262—H262···$Cg2$	0.95	2.89	3.609 (3)	134
C265—H265···$Cg2^{ii}$	0.95	2.89	3.625 (3)	136

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

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059	453 parameters
$wR(F^2)$ = 0.169	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
5790 reflections	$\Delta\rho_{min}$ = −0.31 e Å^{-3}

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic and pyrazole) or 0.98 Å (CH_3) and N—H = 0.88 Å, and with U_{iso}(H) = kU_{eq}(carrier), where k = 1.5 for methyl H atoms, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors thank 'Servicios Técnicos de Investigación of Universidad de Jaén' and the staff for data collection. JP and DE thank Universidad de los Andes for financial support. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén (project reference UJA_07_16_33) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3361). Services for accessing these data are described at the back of the journal.

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