

5-Nitro-*N*⁴,*N*⁶-diphenylpyrimidine-4,6-diamine: polarized molecules linked into π -stacked chains *via* three-centre C—H \cdots (O)₂ hydrogen bonds

Ricaurte Rodríguez,^{a‡} Manuel Noguera,^a Justo Cobo^a and Christopher Glidewell^{b*}

^aDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and ^bSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

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

Received 13 July 2009

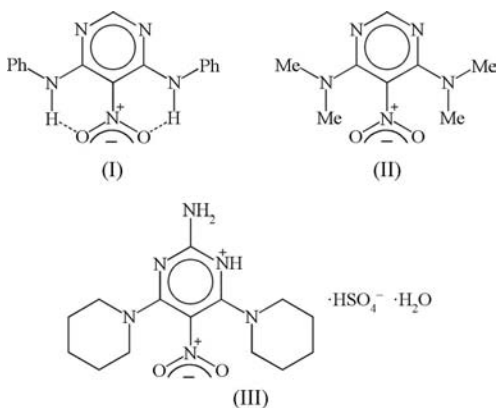
Accepted 24 July 2009

Online 8 August 2009

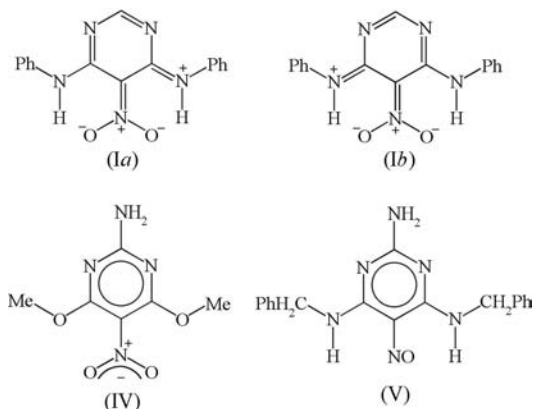
Molecules of the title compound, C₁₆H₁₃N₅O₂, have no internal symmetry despite the symmetric pattern of substitution in the pyrimidine ring. The intramolecular distances indicate polarization of the electronic structure. There are two intramolecular N—H \cdots O hydrogen bonds and molecules are linked into centrosymmetric dimers by pairs of three-centre C—H \cdots (O)₂ hydrogen bonds. These dimers are linked into chains by means of a π – π stacking interaction.

Comment

We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), which we compare with the related compounds (II)–(V) (Makarov *et al.*, 1997; Quesada *et al.*, 2003; Glidewell *et al.*, 2003; Quesada *et al.*, 2004, respectively).



Despite the presence of three adjacent substituents in the pyrimidine ring in (I), this ring is planar within experimental uncertainty; the maximum deviation from the mean plane of the ring is seen for atom N3 [0.007 (2) Å; Fig. 1]. This behaviour may be contrasted with that of the close analogue (II) [Cambridge Structural Database (Allen, 2002) refcode RENTUZ; Makarov *et al.*, 1997], where the pyrimidine ring adopts a boat conformation. The maximum deviation from the mean ring plane in (II) is shown by the C atom corresponding to atom C5 in (I) [0.167 (2) Å], while the nitro N atom is displaced by 1.028 (2) Å to one side of the mean ring plane and the two N atoms of the dimethylamine groups are displaced by 0.411 (2) and 0.443 (2) Å, respectively, to the other side of the ring plane. Similarly, in the cation of (III) (Quesada *et al.*, 2003), where the pyrimidine ring adopts a twist-boat conformation, the N atom of the nitro group is displaced by 1.273 (3) Å to one side of the mean plane of the ring, while the N atoms of the two piperidine substituents are displaced by 0.111 (3) and 0.257 (3) Å to the opposite side of the mean plane. Significant distortion from planarity is, in fact, quite commonly but not invariably observed in highly substituted pyrimidines, particularly in those carrying three adjacent substituents at positions 4, 5 and 6 (Low *et al.*, 2007; Melguizo *et al.*, 2003; Quesada *et al.*, 2003, 2004; Trilleras *et al.*, 2007, 2009; Cobo *et al.*, 2008).



The molecular conformation in (I) can be defined in terms of a small number of torsion angles (Table 1), which indicate that, while the nitro group and one of the phenyl rings (C61–C66) are essentially coplanar with the pyrimidine ring, the other phenyl ring (C41–C46) is markedly displaced from this plane. Thus, the dihedral angles between the plane of the

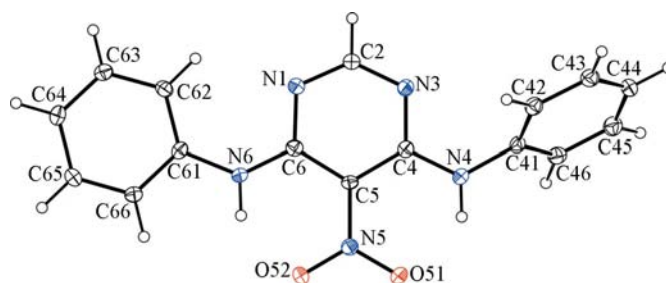


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

[‡] Permanent address: Department of Chemistry, Universidad Nacional de Colombia, Bogotá AA 14490, Colombia.

pyrimidine ring and those of the C41–C46 and C61–C66 rings, respectively, are 60.9 (2) and 1.8 (2)°. Accordingly, the molecule has no internal symmetry, even though the pattern of substituents on the pyrimidine ring permits C_{2v} ($mm2$) molecular symmetry, or either of its subgroups, C_2 or C_s . The fact that the C61–C66 ring is effectively coplanar with the pyrimidine ring indicates that there are no intramolecular factors preventing the adoption of the full molecular symmetry in the crystal. Thus, (I) is an example of a crystal structure in which the molecules exhibit far less than the full molecular symmetry. Perhaps the most familiar example of this phenomenon is benzene, where the unperturbed molecule in the gas phase has D_{6h} ($6/mmm$) symmetry (Kimura & Kubo, 1960), but only a centre of inversion is retained in the crystalline state for both orthorhombic (Cox *et al.*, 1958; Bacon *et al.*, 1964) and monoclinic (Fourme *et al.*, 1971) polymorphs.

The molecule of dimethoxynitropyrimidine (IV) (Glidewell *et al.*, 2003) exhibits no crystallographic symmetry, but the non-H atoms are effectively coplanar, apart from the nitro group, which is twisted out of the ring plane by some 30°, so that this molecule exhibits approximate but noncrystallographic C_2 rotational symmetry. The deviation of the nitro group from the ring plane in (IV) is best attributed to nonbonded electronic repulsions between the O atoms of the nitro group and those of the methoxy groups, in contrast to the attractive N–H···O hydrogen bonds in (I), where the nitro group is effectively coplanar with the pyrimidine ring.

Within the molecule of (I), the C5–N5 bond (Table 1) is very short for its type [mean value (Allen *et al.*, 1987) = 1.468 Å and lower quartile value = 1.460 Å], while the N–O distances are both long (mean value = 1.217 Å and upper quartile value = 1.225 Å); similarly, the C4–N4 and C6–N6 bonds are short for their type (mean value = 1.353 Å and lower quartile value = 1.347 Å), while the C4–C5 and C5–C6 bonds are both long (mean value in pyrimidines = 1.387 Å and upper quartile value = 1.400 Å). These values indicate that polarized forms such as (Ia) and (Ib) are significant contributors to the overall electronic structure in addition to the delocalized aromatic form (I). The corresponding distances in (II) exhibit an exactly analogous pattern of behaviour, showing firstly that the development of polarized forms involving electronic delocalization from amine groups to nitro groups does not depend upon the presence of a planar molecular skeleton, and secondly that the energy cost of evading steric clashes between adjacent substituents by rotation of the amine and nitro groups about the exocyclic C–N bonds, with concomitant loss of the delocalization, exceeds that of distorting the formally aromatic ring. Compound (V) (Quesada *et al.*, 2004) is another close analogue of (I), containing two primary amine substituents, but with a nitroso group rather than a nitro group, so that only one intramolecular N–H···O hydrogen bond is present; again the electronic structure is markedly polarized, with extensive delocalization involving all three amine substituents.

Each of the two independent N–H bonds participates in an intramolecular hydrogen bond (Table 2), forming two edge-fused $S(6)$ motifs (Bernstein *et al.*, 1995), but the N–H bonds

play no role in the intermolecular aggregation. Instead, pairs of molecules are linked into centrosymmetric dimers by means of an asymmetric, but effectively planar, three-centre C–H···(O)₂ hydrogen bond, in which the O51ⁱ··H66··O52ⁱ [symmetry code: (i) $-x, -y + 2, -z + 1$] angle is 51°, giving a sum of angles at H66 of 359°. The dimer thus contains two concentric and centrosymmetric $R_2^2(16)$ motifs together with two symmetry-related $R_1^2(4)$ rings (Fig. 2). These hydrogen-bonded dimers are linked into a chain by a single π – π stacking interaction. The planes of the pyrimidine ring in the molecule at (x, y, z) and the C61–C66 aryl ring in the molecule at $(-x + 1, -y + 1, -z + 1)$ make a dihedral angle of 1.8 (2)°, with an interplanar spacing of *ca* 3.36 Å. The corresponding ring-centroid separation is 3.6500 (15) Å, with a ring-centroid offset of *ca* 1.426 Å. Propagation of this interaction by inversion thus links the hydrogen-bonded dimers centred at $(n, 1 - n, \frac{1}{2})$, where n represents an integer, into a chain running parallel to the $[1\bar{1}0]$ direction (Fig. 2), where pairs of molecules centred across $(\frac{1}{2} + n, \frac{1}{2} - n, \frac{1}{2})$, where n again represents an integer, participate in π – π stacking interactions. Two chains of this type, related to one another by the translational symmetry operations, pass through each unit cell, but there are no direction-specific interactions between the chains; in particular, C–H··· π hydrogen bonds are absent.

It is of interest briefly to compare the one-dimensional supramolecular aggregation in (I) with the corresponding behaviour in the related compounds (II)–(V). In (II) (Makarov *et al.*, 1997), there are no significant direction-specific interactions between the molecules; the closest intermolecular contacts involve methyl C–H bonds. By contrast, in the hydrated salt (III) (Quesada *et al.*, 2003), a combination of three O–H···O hydrogen bonds and three N–H···O hydrogen bonds link the components into a continuous three-dimensional structure, but the anion and solvent components play a dominant role here. Two hydrogen bonds, one each of the N–H···O and N–H···N types, link the molecules of (IV) into sheets built from alternating $R_2^2(8)$ and $R_6^6(32)$ rings (Glidewell *et al.*, 2003). Finally, in (V) (Quesada *et al.*, 2004), two N–H···N hydrogen bonds generate chains of rings, which are linked into sheets by an N–H···O hydrogen bond; these sheets are themselves linked by a C–H···O hydrogen

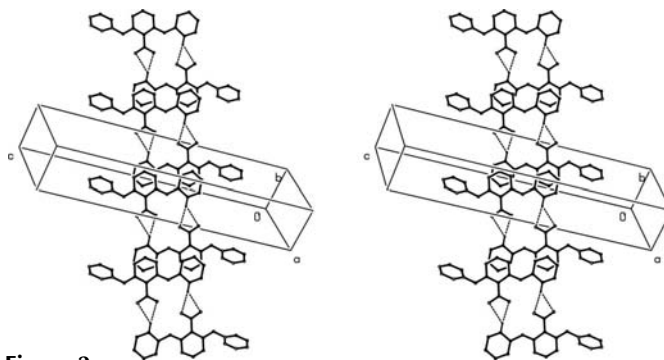


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a chain along $[1\bar{1}0]$ built by the π stacking of hydrogen-bonded dimers. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

bond to form a three-dimensional structure. Thus, in the simple unsolvated compounds (II), (I), (IV) and (V), the supramolecular structures can be regarded as, respectively, zero-, one-, two- and three-dimensional.

Experimental

Aniline (2 mmol) was added dropwise to a solution of 4,6-dichloro-5-nitropyrimidine (1 mmol) in tetrahydrofuran (10 ml) containing triethylamine (0.5 ml), and the resulting reaction mixture was stirred at ambient temperature for 4 h. The mixture was concentrated under reduced pressure, diluted with water and exhaustively extracted with ethyl acetate. The combined organic extracts were washed firstly with aqueous hydrochloric acid (1 mol dm⁻³) and then with brine, and finally dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield the product as a yellow solid (yield 98%, m.p. 441–443 K). Crystals suitable for single-crystal X-ray diffraction were obtained from a solution in dimethyl sulfoxide.

Crystal data

C ₁₆ H ₁₃ N ₅ O ₂	$V = 1344.2 (3) \text{ \AA}^3$
$M_r = 307.31$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.9112 (11) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 5.5582 (6) \text{ \AA}$	$T = 120 \text{ K}$
$c = 30.665 (3) \text{ \AA}$	$0.43 \times 0.21 \times 0.05 \text{ mm}$
$\beta = 94.541 (10)^\circ$	

Data collection

Bruker–Nonius KappaCCD diffractometer	20376 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3094 independent reflections
$T_{\min} = 0.931, T_{\max} = 0.995$	1658 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.084$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	208 parameters
$wR(F^2) = 0.153$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
3094 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Table 1

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

N1–C2	1.319 (3)	C4–N4	1.335 (3)
C2–N3	1.313 (3)	C5–N5	1.410 (3)
N3–C4	1.339 (3)	N5–O51	1.248 (2)
C4–C5	1.418 (3)	N5–O52	1.241 (2)
C5–C6	1.421 (3)	C6–N6	1.332 (3)
C6–N1	1.345 (3)		
N3–C4–N4–C41	–0.2 (4)	N1–C6–N6–C61	–0.6 (4)
C4–N4–C41–C42	61.3 (3)	C6–N6–C61–C62	0.5 (4)
C4–C5–N5–O51	1.0 (3)	C4–C5–N5–O52	–179.2 (2)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H4 \cdots O51	0.88	1.88	2.552 (3)	132
N6–H6 \cdots O52	0.88	1.85	2.569 (3)	137
C66–H66 \cdots O51 ⁱ	0.95	2.59	3.348 (3)	137
C66–H66 \cdots O52 ⁱ	0.95	2.43	3.372 (3)	171

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

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C–H distances of 0.95 \AA and N–H distances of 0.88 \AA , and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{carrier})$.

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: SIR2004 (Burla *et al.*, 2005); 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 the data collection. JC and MN thank the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain), the Universidad de Jaén (project reference UJA_07_16_33) and Ministerio de Ciencia e Innovación (project reference SAF2008-04685-C02-02) for financial support. RR thanks COLCIENCIAS and Universidad Nacional for financial support, and Fundación Carolina for a fellowship to carry out postgraduate studies at the Universidad de Jaén.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3208). Services for accessing these data are described at the back of the journal.

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