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1-(6-Amino-1,3-benzodioxol-5-yl)-3-(4-pyridyl)prop-2-en-1-one crystallizes with Z' = 2: hydrogen-bonded supramolecular substructures in one and two dimensions, each containing only one type of molecule

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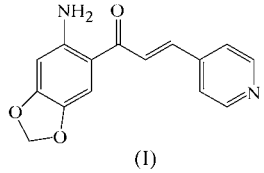
The title compound, $C_{15}H_{12}N_2O_3$, crystallizes with $Z' = 2$ in the space group $P\overline{1}$ and the intramolecular dimensions show evidence for a polarized molecular–electronic structure. Each of the two independent types of molecule forms its own hydrogen-bonded supramolecular substructure, and these are entirely different from one another: one type of molecule forms a chain of edge-fused rings, while the other type forms sheets.

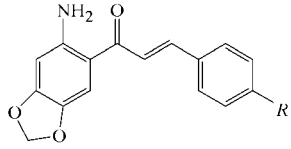
Comment

Intramolecular cyclization of 2-amino-*Z*-chalcones is nowadays one of the most expeditious methods for the synthesis of the biologically significant 2-aryl-2,3-dihydroquinolin-4(1*H*)-ones (Ahmed & van Lier, 2006, 2007; Low, Cobo, Cuervo *et al.*, 2004). We report here the molecular and supramolecular structure of the title compound, (I), as a new example of this class of compound. We have recently reported the structures of the analogues (II)–(VI) (see scheme), which all exhibit completely different modes of supramolecular aggregation (Low *et al.*, 2002; Low, Cobo, Nogueras *et al.*, 2004). In compound (I), the supramolecular structure proves to be different from all examples previously studied.

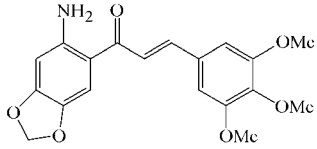
Compound (I) crystallizes with $Z' = 2$ in the space group $P\overline{1}$. The two independent molecules (Fig. 1) are both nearly planar, as shown by the leading torsion angles (Table 1), with the sole exception of the five-membered rings, which both adopt envelope conformations folded across the O···O vectors. The ring-puckering parameters φ (Cremer & Pople, 1975) for the atom sequences O1*n*, C*n*2, O*n*3, C*n*3a, C*n*7a (where n = 1 or 2) are 212.2 (6)° when n = 1 and 30.6 (5)° when n = 2, so that the two molecules within the selected asymmetric unit are approximately mirror images of one another.



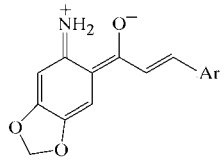
(I)



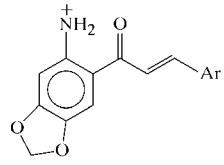
(II) R=Me
(III) R=OMe
(IV) R=CF_3
(V) R=NMe_2



(VI)



A



B

The bond distances in the two independent molecules are very similar (Table 1) and they provide evidence for significant bond fixation within the aminoaryl rings. For example, the C*n*3a—C*n*4 and C*n*7—C*n*7a bonds (where n = 1 or 2) are all short, while the C*n*5—C*n*6 and C*n*6—C*n*7 bonds are all long. In addition, the C*n*6—C*n*8 bonds are short for their type, while the C*n*8—O*n*8 bonds are long. This pattern of behaviour closely mimics that in compounds (II)–(VI) and indicates the importance of the charge-separated form *A* as an important contributor to the overall molecular-electronic structure, alongside the delocalized form *B*.

In each of the two molecules of (I), there is an intramolecular N—H···O hydrogen bond (Table 2). The actions of the intermolecular hydrogen bonds generate two entirely different substructures, one composed solely of type 1 molecules and other entirely of type 2 molecules. In the type 1 substructure, amino atom N15 in the type 1 molecule at (x, y, z) acts as hydrogen-bond donor to pyridyl atom N114 in the type 1 molecule at (x, 1 + y, 1 + z), so generating by translation a $C(11)$ chain (Bernstein *et al.*, 1995) running parallel to the [011] direction. In addition, aryl atom C116 at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O18 in the type 1 molecule at (1 − x, 2 − y, 1 − z), so generating by inversion an $R_2^2(14)$ ring centred at ($\frac{1}{2}$, 1, $\frac{1}{2}$). The combination of these two motifs then generates a chain of edge-fused rings along [011], with $R_2^2(14)$ rings centred at ($\frac{1}{2}$, n, $n - \frac{1}{2}$) (n = zero or integer), and $R_4^4(20)$ rings, alternatively described as $R_6^4(16)$ rings if the intramolecular hydrogen bond is included, centred at ($\frac{1}{2}$, $n + \frac{1}{2}$, n) (n = zero or integer) (Fig. 2).

In contrast with the one-dimensional substructure formed by the type 1 molecules, the substructure built from type 2 molecules is two-dimensional. Atom N25 in the type 2 molecule at (x, y, z) acts as hydrogen-bond donor to pyridyl atom

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N214 in the type 2 molecule at $(x, 1 + y, 1 + z)$, so forming by translation a $C(11)$ chain along [011], exactly analogous to that formed by the type 1 molecules. In addition, atom C22 at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O28 in the type 2 molecule at $(-1 + x, y, z)$, so generating by translation a $C(8)$ chain running parallel to the [100] direction. The combination of the [100] and [011] chains generates a sheet lying parallel to $(01\bar{1})$ and containing equal numbers of $S(6)$ and $R_5^4(33)$ rings (Fig. 3).

Thus, the two types of molecule in compound (I) form substructures which are entirely different. There are no direction-specific interactions between adjacent chains of type 1 molecules, or between adjacent sheets of type 2 molecules, nor are there any direction-specific interactions between the two different substructures. Instead, the type 1 chains simply lie between pairs of type 2 sheets.

Two other members of this series also crystallize with $Z' = 2$. In compound (V) (Low *et al.*, 2002), the two independent molecules are linked by N—H···O hydrogen bonds to form cyclic centrosymmetric tetramers containing two molecules of each type, and the tetramers are further linked into chains by C—H···O hydrogen bonds. Compound (III) exhibits concomitant polymorphism as it crystallizes from solution in dimethylformamide as a mixture of monoclinic ($Z' = 1$) and triclinic ($Z' = 2$) crystals (Low, Cobo, Nogueras *et al.*, 2004). In the polymorph having $Z' = 2$, one type of molecule forms a simple chain and the other type is pendent from it. Neither of compounds (III) and (V) with $Z' = 2$ contains two distinct substructures analogous to those found here in compound (I).

For none of compounds (I)–(V), which differ only in the identity of a single substitution in an aryl ring, could the supramolecular structure of any single example be reliably predicted from a detailed knowledge of the supramolecular structures of the remainder. Not even the type of direction-specific intermolecular interaction manifest in each structure is readily predictable. The wide range of supramolecular structures observed in this series, combined on the one hand with the occurrence of two completely distinct and independent substructures formed by the two independent molecules in compound (I) and, on the other, with the occurrence of concomitant polymorphism in compound (III), together present a very keen challenge to the attempted prediction from first principles of the crystal structures, dominated by weak direction-specific intermolecular forces, of simple molecular compounds, an endeavour where convincing success is still elusive (Lommerse *et al.*, 2000; Motherwell *et al.*, 2002; Day *et al.*, 2005).

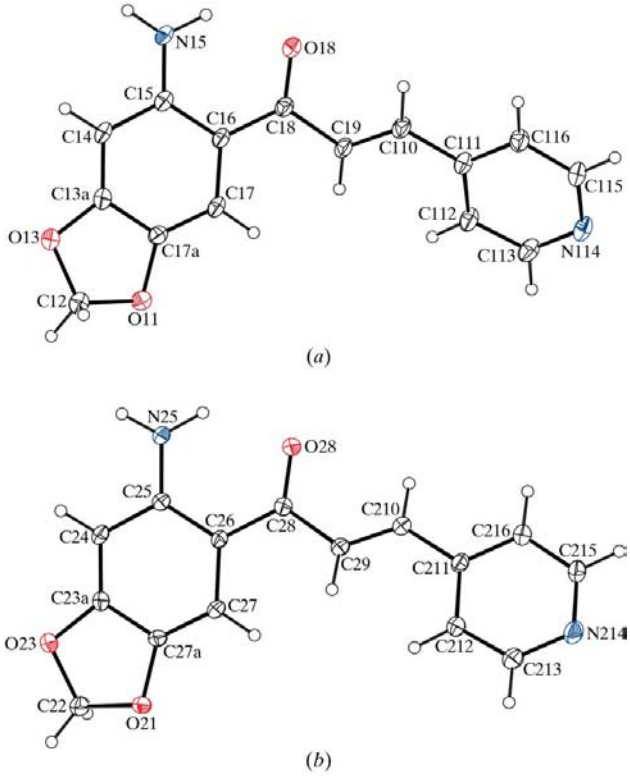

Figure 1
The two independent molecules of compound (I), showing the atom-labelling scheme for (*a*) a type 1 molecule and (*b*) a type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

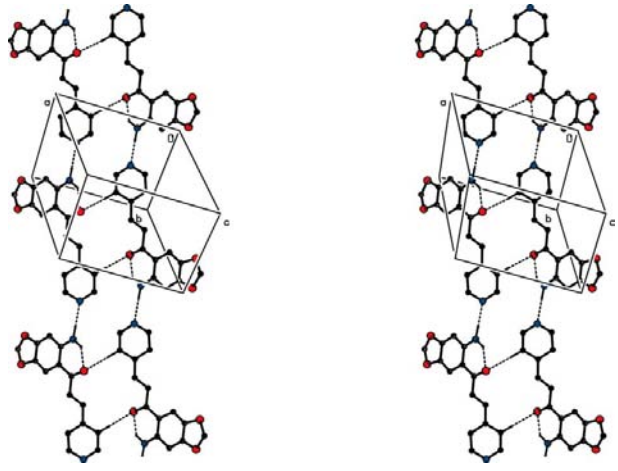

Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of edge-fused rings along [011] containing only type 1 molecules.

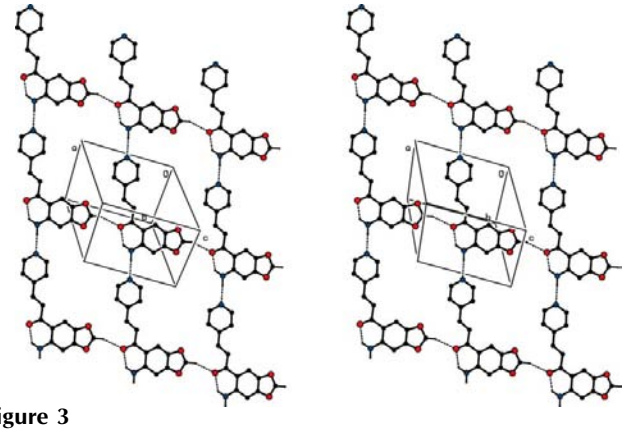

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a sheet parallel to $(01\bar{1})$ containing only type 2 molecules.

Experimental

A solution in ethanol (10 ml) of 6-amino-3,4-methylenedioxyacetophenone (2.8 mmol), pyridine-4-carbaldehyde (2.8 mmol) and aqueous sodium hydroxide solution (0.5 ml of a 20% solution) was stirred at room temperature for 3 h. The precipitate thus formed was collected by filtration and washed with ethanol, yielding compound (I) as an orange solid (yield 70%; m.p. 469 K). MS (70 eV) *m*/e (%): 268 (50, $[M]^+$), 190 (100, $[M - C_5H_4N]^+$). Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Crystal data

$C_{15}H_{12}N_2O_3$
M_r = 268.27
Triclinic, $P\overline{1}$
a = 10.1044 (3) Å
b = 11.7533 (5) Å
c = 12.1655 (5) Å
α = 117.232 (2)°
β = 97.480 (3)°
γ = 99.585 (2)°
V = 1231.11 (9) Å^3
Z = 4
D_x = 1.447 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 (2) K
Lath, orange
0.44 × 0.38 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.967, T_{max} = 0.993
28373 measured reflections
5675 independent reflections
3599 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 27.7°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.169
S = 1.03
5675 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 0.3836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C13a—C14	1.364 (3)	C23a—C24	1.353 (3)
C14—C15	1.427 (3)	C24—C25	1.426 (3)
C15—C16	1.428 (3)	C25—C26	1.428 (3)
C16—C17	1.425 (3)	C26—C27	1.426 (3)
C17—C17a	1.357 (3)	C27—C27a	1.354 (3)
C17a—C13a	1.390 (3)	C27a—C23a	1.394 (3)
C15—N15	1.356 (3)	C25—N25	1.351 (3)
C16—C18	1.459 (3)	C26—C28	1.467 (3)
C18—O18	1.242 (3)	C28—O28	1.242 (2)
C15—C16—C18—C19	176.55 (19)	C25—C26—C28—C29	171.38 (18)
C16—C18—C19—C110	−152.2 (2)	C26—C28—C29—C210	165.6 (2)
C18—C19—C110—C111	−179.3 (2)	C28—C29—C210—C211	179.56 (19)
C19—C110—C111—C112	9.0 (4)	C29—C210—C211—C212	2.8 (3)

Crystals of compound (I) are triclinic. The space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 (aromatic and alkenic) or 0.99 Å (CH_2) and N—H = 0.96 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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).

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

D—H···A	D—H	H···A	D···A	D—H···A
N15—H15A···O18	0.96	1.90	2.657 (3)	134
N15—H15B···N114^{i}	0.96	2.09	3.054 (3)	179
C116—H116···O18^{ii}	0.95	2.55	3.430 (3)	154
N25—H25A···O28	0.96	1.94	2.662 (2)	130
N25—H25B···N214^{i}	0.96	2.04	2.996 (3)	176
C22—H22A···O28^{iii}	0.99	2.41	3.270 (3)	145

Symmetry codes: (i) $x, y+1, z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $x-1, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3063). Services for accessing these data are described at the back of the journal.

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