

1-(2-Aminophenyl)-3-(4-pyridyl)prop-2-en-1-one: a three-dimensional framework structure built from N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds

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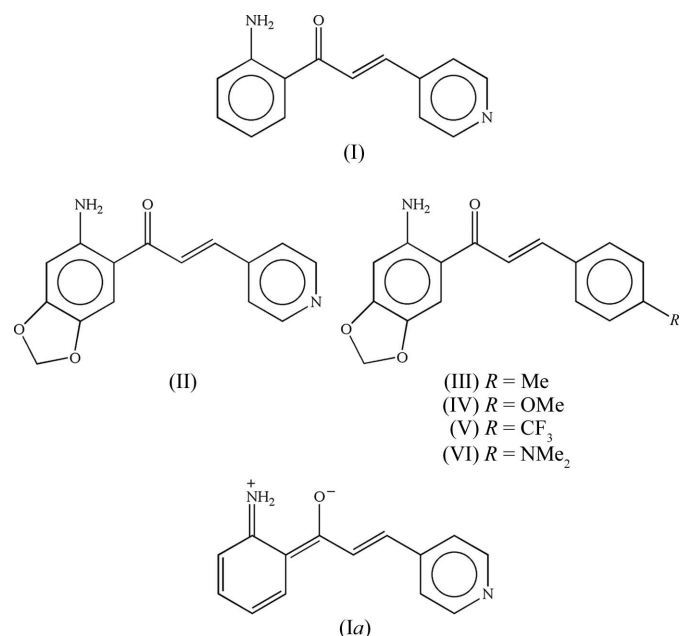
The intramolecular dimensions of the title compound, C₁₄H₁₂N₂O, provide evidence for a polarized electronic structure. The molecule, which is almost completely planar, contains an intramolecular N—H···O hydrogen bond, and the molecules are linked by a combination of N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds to form a three-dimensional framework structure.

Comment

Chalcones (1,3-diarylpropenones) are very versatile synthetic intermediates (Awad *et al.*, 1960; Carrie & Rochard, 1963; Coudert *et al.*, 1988; Insuasty *et al.*, 1992, 1997; Kolos *et al.*, 1996). We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), which we compare with the structure of the related compound 1-(6-amino-1,3-benzodioxol-5-yl)-3-(4-pyridyl)prop-2-en-1-one, (II) (Cuervo *et al.*, 2007), which is itself closely related to the series of compounds (III)–(V) (Low *et al.*, 2004) and (VI) (Low *et al.*, 2002) (see scheme). 2-Amino-chalcones are key intermediates in the synthesis of 6,7-methylenedioxytetrahydroquinolin-4-ones, compounds with interesting biological and pharmacological properties (Prager & Thredgold, 1968; Donnelly & Farrell, 1990; Kurasawa *et al.*, 2002), while more generally, many compounds, both synthetic and naturally occurring, containing the 1,3-dioxolyl group are of importance because of their pharmacological properties (Krause & Goeber, 1972; Ohta & Kimoto, 1976; Ma *et al.*, 1987; Gabrielsen *et al.*, 1992).

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Compound (I) crystallizes in the space group *C2/c* with $Z' = 1$, whereas the closely related compound (II) crystallizes with $Z' = 2$ in the space group $P\bar{1}$, where the pattern of hydrogen bonding clearly rules out any possibility of additional crystallographic symmetry (Cuervo *et al.*, 2007). The molecule of (I) is very nearly planar, as indicated by the key torsion angles (Table 1). For the molecular fragment between atoms C11 and N34 (Fig. 1), the maximum deviations from the mean plane through the non-H atoms are 0.069 (2) Å for atom O1 and 0.050 (2) Å for atom C11. The dihedral angle between this plane and that of the C11–C16 ring is only 8.62 (9)°. As in compounds (II)–(VI) (Cuervo *et al.*, 2007; Low *et al.*, 2004), there is an intramolecular N—H···O hydrogen bond in (I), forming an *S*(6) motif (Bernstein *et al.*, 1995), and this may have some influence on the overall molecular conformation.



A more significant factor influencing the conformation of (I) may be the electronic polarization indicated by the intramolecular distances (Table 1). Within the C11–C16 ring, the C13–C14 and C15–C16 distances are significantly shorter than the other C–C distances, indicating some degree of *o*-quinonoid bond fixation. In addition, the exocyclic bonds

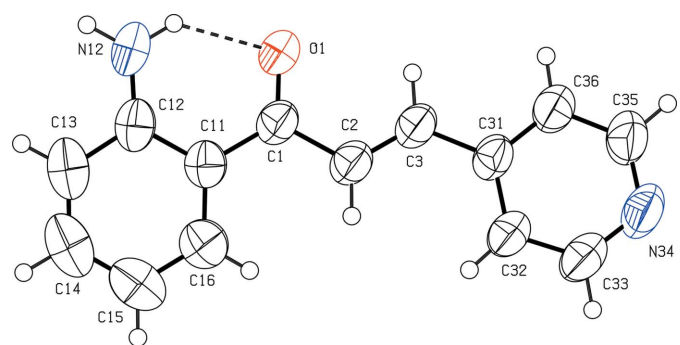
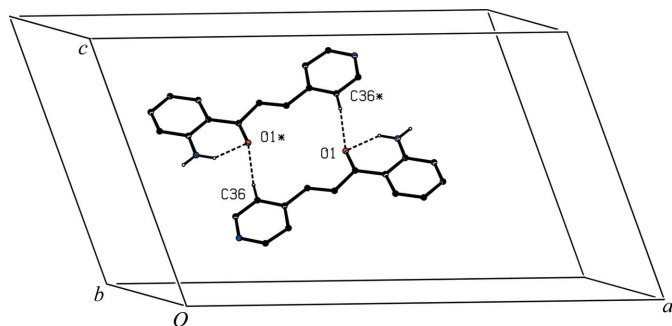


Figure 1

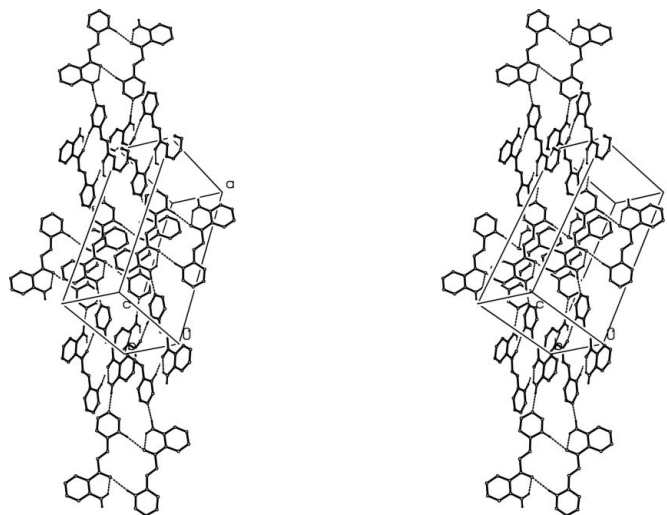
The molecular structure of (I), showing the atom-labelling scheme and the intramolecular N—H···O hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 50% probability level.


Figure 2

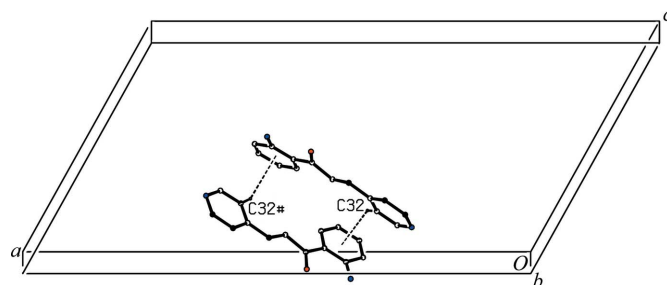
Part of the crystal structure of (I), showing the formation of a cyclic centrosymmetric dimer built from paired C—H···O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 2 - y, 1 - z)$.

C12—N12 and C11—C1 are both short for their types [mean values (Allen *et al.*, 1987) = 1.355 and 1.488 Å, respectively; lower quartile values = 1.340 and 1.468 Å, respectively]. Similar patterns were observed for the C—C and C—N distances in each of (II)–(VI) (Cuervo *et al.*, 2007; Low *et al.*, 2002, 2004). However, the C1—O1 distance in (I) is not particularly long compared with those in (II)–(VI), which range from 1.237 (2) to 1.253 (2) Å, with a mean of 1.245 Å, for ten independent values [compounds (II), (V) and (VI) all crystallize with $Z' = 2$, while there are two polymorphs of (IV), one monoclinic and the other triclinic, with $Z' = 1$ and 2, respectively]. These observations indicate the charge-separated form (Ia) as a significant contributor to the overall electronic structure. Form (Ia) is certainly consistent with the near coplanarity observed between the C11—C16 ring and the rest of the molecular structure, despite the rather short intramolecular H2···H16 distance of only 2.04 Å. By way of comparison, the corresponding intramolecular distance involving the pyridyl ring, H2···H32, is somewhat longer at 2.26 Å, even though the pyridyl ring is effectively coplanar with the spacer unit containing atoms C1—C3. It is tempting, therefore, to interpret the orientation of the C11—C16 ring in terms of the competing effects of the intramolecular hydrogen bond and the electronic polarization on the one hand, and a repulsive intramolecular H···H contact on the other.

The molecules of (I) are linked by N—H···N, C—H···O and C—H··· π (arene) hydrogen bonds, the first two of which are almost linear (Table 2). It is convenient to consider as the basic building block in the hydrogen-bonded structure the cyclic centrosymmetric $R_2^2(14)$ dimer unit built from paired C—H···O hydrogen bonds (Fig. 2). The reference dimer is centred at $(\frac{1}{2}, 1, \frac{1}{2})$ and is directly linked, by means of N—H···N hydrogen bonds, to four further dimers, centred at $(0, \frac{1}{2}, 0)$, $(0, \frac{3}{2}, 0)$, $(1, \frac{1}{2}, 1)$ and $(1, \frac{3}{2}, 1)$, so forming a sheet lying parallel to $(10\bar{1})$ (Fig. 3). In addition to the $S(6)$ rings, the sheet contains equal numbers of centrosymmetric large and small rings, arranged alternately in a chess-board fashion. The small rings are of $R_2^2(14)$ type. If the large rings are taken to include the intramolecular hydrogen bond, then they are of $R_{10}^8(38)$ type, otherwise they are of $R_6^6(42)$ type. The C—H··· π (arene) hydrogen bond links a pair of molecules related by a twofold


Figure 3

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet parallel to $(10\bar{1})$ and containing N—H···O, N—H···N and C—H···O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms but not involved in the motifs shown have been omitted.


Figure 4

Part of the crystal structure of (I), showing the formation of a cyclic dimer built from paired C—H··· π (arene) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. The atom marked with a hash (#) is at the symmetry position $(1 - x, y, \frac{1}{2} - z)$.

rotation axis into another type of cyclic dimer (Fig. 4). The effect of this cyclic motif is to link each $(10\bar{1})$ sheet to the two adjacent sheets, so linking the molecules into a continuous three-dimensional framework structure.

It is of interest briefly to compare the hydrogen-bonded structure of (II) (Cuervo *et al.*, 2007) with that reported here for (I). The close similarity between the molecular constitutions of (I) and (II) might have been expected to lead to some similarities in their modes of intermolecular aggregation, but in fact the aggregation in (I) and (II) is very different. As noted above, (II) crystallizes with $Z' = 2$, and each of the two independent molecules is linked by a combination of N—H···N and C—H···O hydrogen bonds, just as in (I), although C—H··· π (arene) hydrogen bonds are absent from the structure of (II). However, each of the independent molecules forms an independent substructure, with no hydrogen bonds between molecules of the two types. More striking is the difference between the two substructures: one consists of a chain of edge-fused $R_2^2(14)$ and $R_6^4(16)$ rings, while the other consists of sheets containing equal numbers of $S(6)$ and $R_5^4(33)$

rings (Cuervo *et al.*, 2007). Thus, the only point of similarity between the hydrogen-bonded structures of (I) and (II) lies in the formation of centrosymmetric $R_2^2(14)$ rings containing paired C—H \cdots O hydrogen bonds, as formed by (I) and by one of the molecular types in (II). It is thus worth emphasizing that the molecular constitutions of (I) and (II) differ only by the presence in (II) of a fused dioxolane ring, which does not occupy any of the hydrogen-bonding sites utilized in (I). While this additional ring participates in sheet formation in (II), it plays no role in the formation of the chain of edge-fused rings. This chain in (II) is built from two hydrogen bonds, one each of N—H \cdots N and C—H \cdots O types, which utilize exactly the same atoms as donors and acceptors as those in (I), except that these hydrogen bonds are mediated by different symmetry operators in the two compounds, consequent upon their different space groups.

Experimental

A mixture of 2'-aminoacetophenone (2.8 mmol), pyridine-4-carbaldehyde (2.8 mmol), ethanol (10 ml) and 20% aqueous sodium hydroxide solution (0.5 ml) was heated under reflux for 20 min. The mixture was cooled to ambient temperature, and the resulting solid precipitate was collected by filtration, washed successively with ethanol (2 \times 0.5 ml) and water (2 \times 0.5 ml), and finally dried under reduced pressure to yield the title compound as an orange solid (yield 82%; m.p. 440 K). MS (70 eV) m/z (%): 224 (23) (M^+), 223 (12), 195 (8), 146 (100). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, of a solution in ethanol.

Crystal data

$C_{14}H_{12}N_2O$	$V = 2305.2$ (8) \AA^3
$M_r = 224.26$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 27.922$ (6) \AA	$\mu = 0.08$ mm^{-1}
$b = 6.4261$ (8) \AA	$T = 296$ K
$c = 14.668$ (3) \AA	$0.30 \times 0.17 \times 0.16$ mm
$\beta = 118.849$ (18) $^\circ$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	17566 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2141 independent reflections
$T_{\min} = 0.954$, $T_{\max} = 0.987$	1403 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	154 parameters
$wR(F^2) = 0.126$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.13$ e \AA^{-3}
2141 reflections	$\Delta\rho_{\text{min}} = -0.15$ e \AA^{-3}

All H atoms were located in difference maps and then treated as riding. H atoms bonded to C atoms were permitted to ride in geometrically idealized positions, with C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms bonded to atom N12 were permitted to ride at the positions deduced from the difference maps, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, giving N—H = 0.88 \AA .

Data collection: COLLECT (Nonius, 1999); cell refinement: DIRAX/LSQ (Duisenberg *et al.*, 2000); data reduction: EVALCCD

Table 1

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

C11—C12	1.409 (3)	C12—N12	1.331 (3)
C12—C13	1.395 (3)	C1—C11	1.452 (3)
C13—C14	1.338 (3)	C1—O1	1.224 (2)
C14—C15	1.374 (3)	C1—C2	1.473 (2)
C15—C16	1.356 (3)	C2—C3	1.299 (2)
C16—C11	1.392 (3)	C3—C31	1.451 (2)
C12—C11—C1—C2	169.49 (17)	C1—C2—C3—C31	-178.49 (18)
C11—C1—C2—C3	-178.21 (18)	C2—C3—C31—C32	2.6 (3)

Table 2

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

Cg1 represents the centroid of the C11—C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N12—H12A \cdots O1	0.88	1.93	2.621 (3)	134
N12—H12B \cdots N34 ⁱ	0.88	2.10	2.982 (3)	174
C36—H36 \cdots O1 ⁱⁱ	0.93	2.36	3.283 (3)	170
C32—H32 \cdots Cg1 ⁱⁱⁱ	0.93	2.87	3.611 (3)	137

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $-x + 1, y, -z + \frac{1}{2}$.

(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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3062). Services for accessing these data are described at the back of the journal.

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