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1-(6-Amino-1,3-benzodioxol-5-yl)-3-(2-oxo-1,2-dihydroquinolin-3-yl)prop-2-enone: a sheet built by π-stacking of hydrogen-bonded chains of rings

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The bond distances in the molecule of the title compound, $C_{19}H_{14}N_2O_4$, provide evidence for electronic polarization in the aminoarylpropenone fragment and for bond fixation in the quinolinone unit. Molecules are linked by N—H···O and C—H···O hydrogen bonds into chains in which centrosymmetric rings of $R_2^2(8)$ and $R_2^2(18)$ types alternate, and these chains are linked into sheets by a single aromatic π–π stacking interaction.

Comment

We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1). Dioxolotetrahydroquinolin-8-one units are found in a number of compounds used as antimitotic and antitumour agents (Prager & Thredgold, 1968; Donnelly & Farell, 1990; Kurasawa *et al.*, 2002; Zhang *et al.*, 2000), and 2-aminochalcones are useful intermediates for the synthesis of such quinolinone derivatives. Several years ago we reported the molecular and supramolecular structures of a number of such 2-aminochalcones (Low, Cobo, Nogueras *et al.*, 2004), *viz.* compounds (II)–(VI) (see scheme), and of some quinolinones formed by their acid-catalysed cyclization (Low, Cobo, Cuervo *et al.*, 2004). Compound (I), in which the terminal substituted aryl group present in compounds (II)–(VI) has been replaced by a 2-oxoquinolin-3-yl unit, was prepared by a base-catalysed condensation between an acetophenone and an aldehyde, for use as an intermediate in the synthesis of the corresponding dihydroquinolin-8-one by 6-*endo* intramolecular cyclization (Low, Cobo, Cuervo *et al.*, 2004; Abonía *et al.*, 2008).

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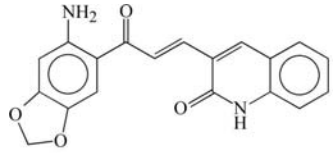
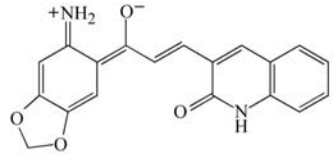
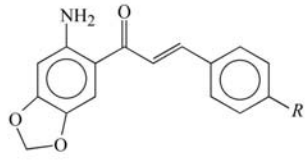
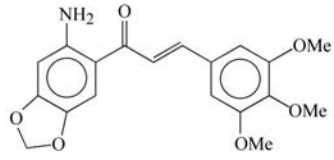
Compound (I) crystallizes with $Z' = 1$, as do (II), (VI) and the monoclinic polymorph of (III) (Low, Cobo, Nogueras *et al.*, 2004). On the other hand, the triclinic polymorph of (III), and (IV) and (V), all crystallize with $Z' = 2$. No simple explanation of this behaviour presents itself. Within the molecule of (I), the spacer unit joining the two ring systems adopts an effectively planar all-*trans* configuration, and the two adjacent rings are almost coplanar with the spacer unit, as shown by the key torsion angles (Table 1). This planarity permits, but not does require, extensive electronic delocalization. The sole exception to the skeletal planarity is found in the dioxolane ring, where atom C12 is modestly displaced by 0.057 (2) Å from the mean plane of this ring, corresponding to an envelope fold across the O11···O13 line.


(I)


(Ia)


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


(VI)

In the C13a/C14–C17/C17a aryl ring, the C13a—C14 and C17—C17a bonds are both significantly shorter than the other

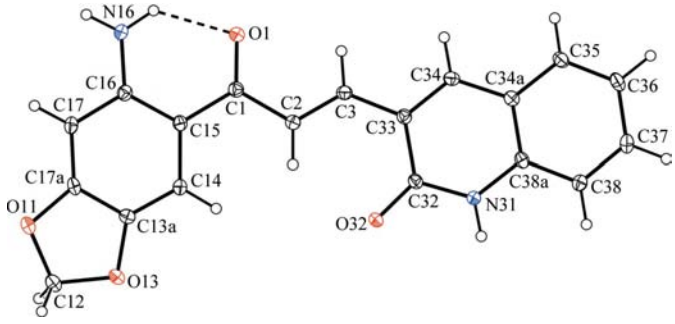


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and the intramolecular hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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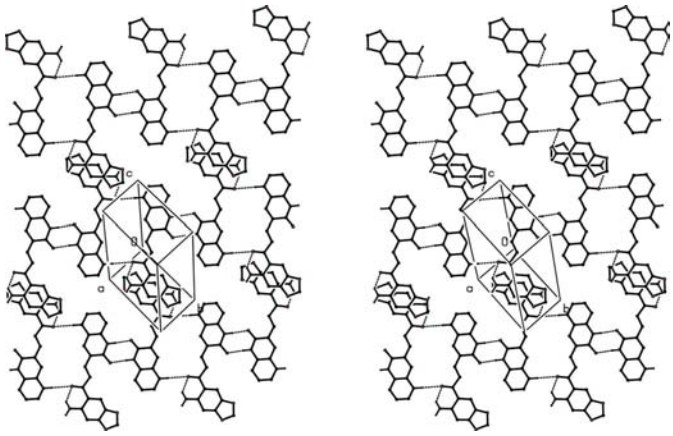

Figure 2
A stereoview of part of the crystal structure of (I), showing the π-stacking of hydrogen-bonded chains along [2$\bar{1}$0] to form a sheet parallel to (122). For the sake of clarity, H atoms bonded to C atoms which are not involved in the motifs shown have been omitted.

four C—C distances in this ring (Table 1). At the same time, the C1—O1 bond is long for its type [mean value (Allen *et al.*, 1987) = 1.222 Å] and the C1—C15 bond is short for its type (mean value = 1.488 Å). The C15—C16 bond is one of the longer ones in this aryl ring, and the C16—N16 bond is also short for its type (mean value = 1.394 Å, lower quartile value = 1.385 Å). Similar patterns of distances were observed in the corresponding molecular fragments in compounds (II)–(VI) (Low, Cobo, Nogueras *et al.*, 2004). The C—C distances in the quinoline portion of the molecule provide evidence for bond fixation, as the C35—C36 and C37—C38 bonds are shorter than the other bonds in this carbocyclic ring. These observations, taken as a whole, indicate that form (I*a*) is a significant contributor to the overall electronic structure, in addition to form (I), although there appears to be no electronic delocalization between the two ring systems despite the planarity of the molecular skeleton.

There is an intramolecular hydrogen bond (Table 2) forming an *S*(6) motif (Bernstein *et al.*, 1995) which may be regarded as charge-assisted (Gilli *et al.*, 1994), but the second N—H bond of the amino group plays no role in the intermolecular hydrogen bonding, as there is no potential acceptor within plausible hydrogen-bonding distance. Instead, the molecules are linked by one N—H···O hydrogen bond, using the quinolinone N—H bond, and one C—H···O hydrogen bond, both almost linear (Table 2), into a chain containing two types of centrosymmetric ring. Rings of $R_2^2(8)$ type built from paired N—H···O hydrogen bonds are centred at ($2n - \frac{1}{2}$, $-n + \frac{1}{2}$, $\frac{1}{2}$), where n represents an integer, and these alternate with $R_2^2(18)$ rings built from paired C—H···O hydrogen bonds and centred at ($2n + \frac{1}{2}$, $-n$, $\frac{1}{2}$), where n again represents an integer, so forming a chain running parallel to the [2$\bar{1}$0] direction (Fig. 2).

A single aromatic π–π stacking interaction links, albeit fairly weakly, the hydrogen-bonded chains into a sheet. Rings C13a/C14–C17/C17a in the molecules at (x, y, z) and ($1 - x$, $-y$, $1 - z$) are strictly parallel, with an interplanar spacing of 3.641 (2) Å. The ring centroid separation is 3.812 (2) Å, corresponding to a ring-centroid offset of 1.131 (2) Å. The effect of this interaction, when propagated by inversion, is to link the chains parallel to [2$\bar{1}$0] into a sheet parallel to (122) (Fig. 2), but there are no direction-specific interactions between adjacent sheets. In this context, it is interesting to note that not only does the amino group play no role in the intermolecular aggregation, but neither do atoms O11 and O13.

The formation of sheets generated by the π-stacking of hydrogen-bonded chains was also observed in (IV) and (VI) (Low, Cobo, Nogueras *et al.*, 2004), although in each of these structures the chains are simple chains of *C*(7) and *C*(10) types, as opposed to the chains of rings observed here in (I). In both (II) and the monoclinic polymorph of (III), a combination of N—H···O and C—H···π(arene) hydrogen bonds forms the sheet structures directly, without any π–π stacking. By contrast, in the triclinic polymorph of (III), the structure is built from simple *C*(8) chains without any π–π stacking, while in (V) the molecules are linked by N—H···O hydrogen bonds into centrosymmetric tetramers. Thus, within this series of compounds, (I)–(VI), the hydrogen-bonding can give rise to aggregation in zero, one or two dimensions. This variation, combined with the differing Z' values, points to considerable structural diversity within this series of rather closely related compounds.

Experimental

A mixture of 1-(6-amino-1,3-benzodioxol-5-yl)ethanone (0.50 g, 2.8 mmol) and 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (0.48 g, 2.8 mmol) in ethanol (10 ml) containing 20% (*w*/*v*) aqueous sodium hydroxide solution (0.5 ml) was heated under reflux for 10 min. The mixture was cooled to ambient temperature, and the resulting solid precipitate was collected by filtration, washed successively with ethanol (3 ml) and water (3 ml), and then dried under reduced pressure to give the title compound, (I), in 55% yield. Dark-red crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, from a solution of (I) in dimethylformamide (m.p. 524 K). EIMS (70 eV), *m*/*z* (%): 334 (12 [M^+]), 333 (62 [$M - 1$]), 190 (23, [$M - C_9H_6N$]). Analysis found: C 68.3, H 4.1, N 8.3%; $C_{19}H_{14}N_2O_4$ requires: C 68.3, H 4.2, N 8.4%.

Crystal data

$C_{19}H_{14}N_2O_4$
M_r = 334.32
Triclinic, $P\bar{1}$
a = 5.7799 (2) Å
b = 9.9485 (3) Å
c = 13.0849 (5) Å
α = 83.343 (2)°
β = 86.652 (2)°
γ = 77.128 (2)°
V = 728.13 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 K
0.10 × 0.06 × 0.06 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.989, T_{max} = 0.994
9539 measured reflections
2858 independent reflections
2377 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Table 1
Selected geometric parameters (Å, °).

C13a—C14	1.359 (2)	N31—C32	1.364 (2)
C14—C15	1.430 (2)	C32—C33	1.469 (2)
C15—C16	1.423 (2)	C33—C34	1.368 (2)
C16—C17	1.416 (2)	C34—C34a	1.426 (2)
C17—C17a	1.363 (2)	C34a—C35	1.410 (2)
C13a—C17a	1.386 (2)	C35—C36	1.368 (2)
C16—N16	1.375 (2)	C36—C37	1.406 (2)
C15—C1	1.472 (2)	C37—C38	1.375 (2)
C1—O1	1.2403 (19)	C38—C38a	1.398 (2)
C1—C2	1.483 (2)	C38a—N31	1.3777 (19)
C2—C3	1.340 (2)	C34a—C38a	1.403 (2)
C3—C33	1.453 (2)	C32—O32	1.2488 (18)
C1—C2—C3—C33	−179.29 (14)	C2—C1—C15—C14	−7.9 (2)
C2—C3—C33—C32	3.3 (3)	C12—O13—C13a—C14	−178.72 (16)
C3—C2—C1—C15	176.75 (14)	C12—O11—C17a—C17	176.21 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N16—H16*B*···O1	0.91 (2)	1.90 (2)	2.620 (2)	135 (2)
N31—H31···O32^{i}	0.88	1.89	2.768 (2)	176
C35—H35···O1^{ii}	0.95	2.38	3.334 (2)	177

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
2858 reflections	
232 parameters	

All H atoms were located in difference maps. The coordinates of the H atoms bonded to N16 were refined without restraint, with U_{iso}(H) = 1.2U_{eq}(N), giving N—H distances of 0.89 (2) and 0.91 (2) Å, and a sum of the bond angles at N16 of *ca* 349°. The remaining H atoms were treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic or alkenyl) or 0.99 Å (CH_2) and N—H = 0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *COLLECT* (Nonius, 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3356). Services for accessing these data are described at the back of the journal.

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