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A comparison of the supramolecular structures of 1-(6-amino-1,3-benzodioxol-5-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one and 1-(6-amino-1,3-benzodioxol-5-yl)-3-[4-(*N*,*N*-dimethylamino)phenyl]prop-2-en-1-one

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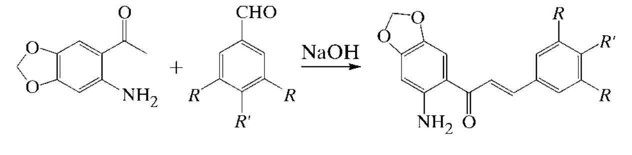
1-(6-Amino-1,3-benzodioxol-5-yl)-3-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one, $C_{19}H_{19}NO_6$, (I), contains an intramolecular N—H···O hydrogen bond and a weak C—H···O hydrogen bond, which forms a $C(10)$ chain motif running parallel to the *c* axis. The 6-amino-1,3-benzodioxol-5-yl moieties are involved in π–π stacking. 1-(6-Amino-1,3-benzodioxol-5-yl)-3-[4-(*N*,*N*-dimethylamino)phenyl]prop-2-en-1-one, $C_{18}H_{18}N_2O_3$, (II), crystallizes with two molecules in the asymmetric unit. The main feature of the supramolecular structure of (II) is the formation of a centrosymmetric hydrogen-bonded tetramer with an $R_8^4(16)$ motif.

Comment

Many synthetic or naturally occurring compounds containing the 1,3-dioxolyl group are very important because of their pharmacological properties (Ma *et al.*, 1987; Ohta & Kimoto, 1976; Schlunke & Egli, 1972; Krause & Goeber, 1972; Gabrielsen *et al.*, 1992). Chalcones (1,3-diarylpropenones) have been widely used as starting materials in numerous synthetic reactions (Awad *et al.*, 1960; Coudert *et al.*, 1988; Carrie & Rochard, 1963), including the preparation of fused-ring heterocyclic compounds (Insuasty *et al.*, 1992, 1997; Kolos *et al.*, 1996). We have prepared the title compounds, (I) and (II), as intermediates in the synthesis of novel dihydroquinolinones. This is a class of compounds with interesting pharmaceutical properties (Pfizer, 1980; Jordis *et al.*, 1991; Baker *et al.*, 1990), since the 1,3-dioxolyl residue in their frameworks enhances their practical applications.



R, *R*′=OMe
R=H, *R*′=NMe$_2$

(I) *R*, *R*′=OMe
(II) *R*=H, *R*′=NMe$_2$

The molecular structures of (I) and the two independent molecules of (II) are shown in Figs. 1 and 2, respectively. The

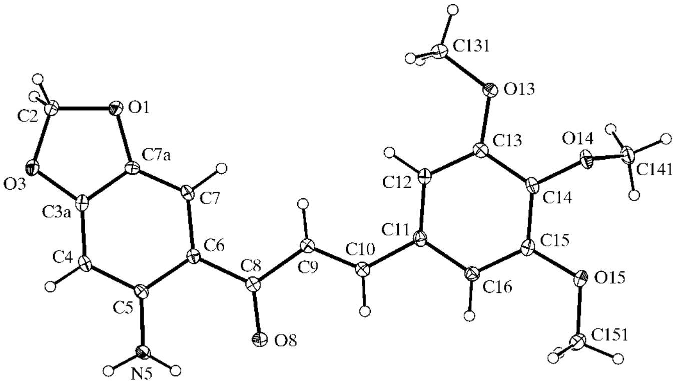


Figure 1
A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

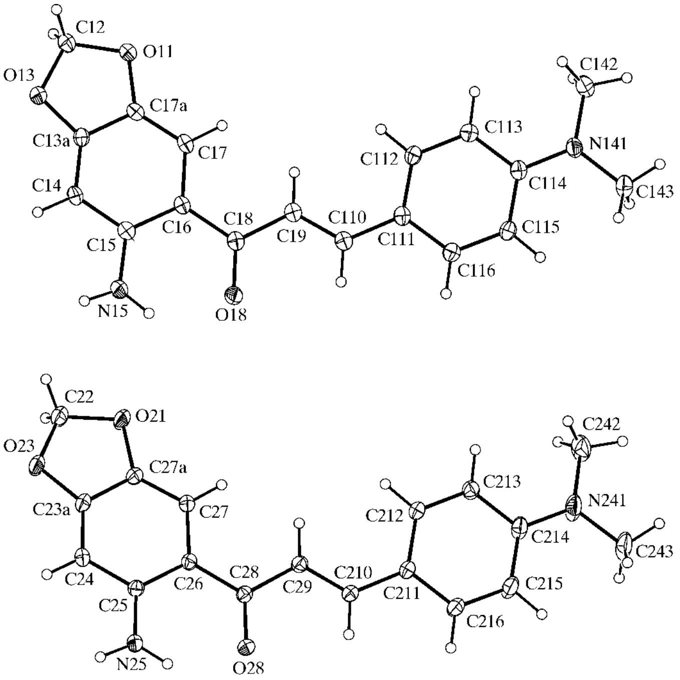


Figure 2
Views of the two independent molecules of (II) with the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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dioxol-5-yl groups in all three molecules have *C*2 envelope puckers. In (I), a strong intramolecular hydrogen bond is observed with an *S*(6) motif *via* N5—H5*A*···O8 (Bernstein *et al.*, 1995) (Fig. 1, Table 1), and likewise in (II) *via* N15—H15*A*···O18 and N25—H25*A*···O28 (Fig. 2 and Table 2).

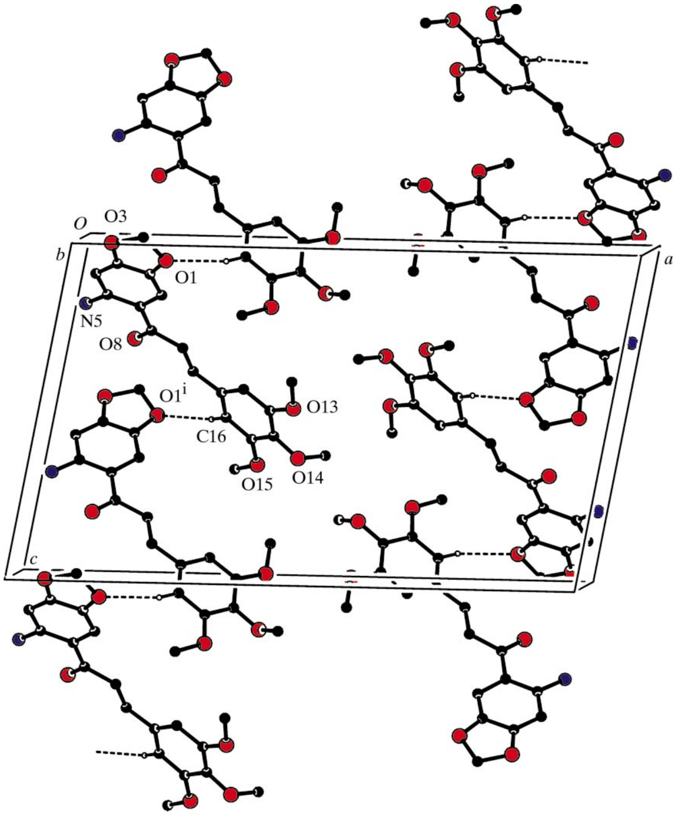

Figure 3
A view of the crystal structure of (I), looking down the *b* axis, showing two anti-parallel *C*(10) chains [symmetry code: (i) $x, -\frac{1}{2} - y, z - \frac{1}{2}$].

The supramolecular structures of (I) and (II) are completely different. In (I), a *C*(10) motif is formed *via* C16—H16···O1$(x, -\frac{1}{2} - y, z - \frac{1}{2})$, creating a chain which runs parallel to the *c* axis. Two such anti-parallel chains are shown in Fig. 3. Atom H5*B* is not involved in any hydrogen bonding. In (II), however, the equivalent H atoms H15*B* and H25*B* are involved in strong hydrogen bonds *via* N15—N15*B*···O28$(1 - x, 1 - y, 1 - z)$ and N25—H25*B*···O18, linking molecules 1 and 2 to form a tetramer with an $R_8^4(16)$ motif (Fig. 4). Such motifs occur centred at $(l + \frac{1}{2}, m + \frac{1}{2}, n + \frac{1}{2})$, where *l*, *m* and *n* are integers or zero. The weak C14—H14···O28$(1 - x, 1 - y, 1 - z)$ and C24—H24···O18 hydrogen bonds help to reinforce this tetramer structure. The tetramers are linked to each other by weak hydrogen bonds *via* C212—H212···O13$(x, y, z - 1)$ and C212$(1 - x, 1 - y, z)$—H212$(1 - x, 1 - y, z)$···O13$(1 - x, 1 - y, 1 - z)$, which form bridging $R_4^4(26)$ rings along with the N15—H15···O28 hydrogen bonds of the tetramer (Fig. 5).

In (I), there is π–π stacking between the benzo-1,3-dioxol-5-yl groups, where the rings defined by O1/C2/O3/C3a/C7a and C3a/C4–C7/C7a are stacked such that the distance between the centres of gravity of the rings is 3.7276 (9) Å, the dihedral angle is 3.50°, the perpendicular distance from the centre of gravity of the former ring at (x, y, z) to the latter at $(x, 1 + y, z)$ is 3.368 Å and the perpendicular distance from the centre of gravity of the latter ring at (x, y, z) to the former at

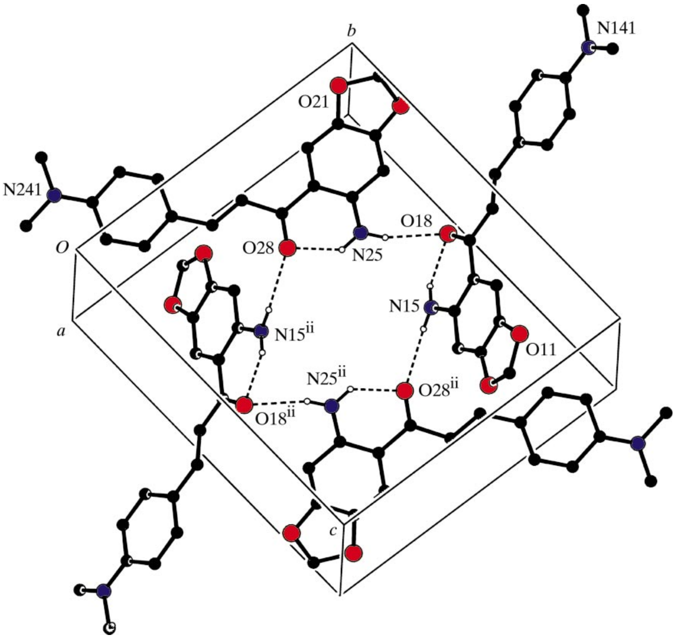

Figure 4
A view of the tetramer formed by the molecules of (II) at (x, y, z) and $(1 - x, 1 - y, 1 - z)$. For the sake of clarity, H atoms bonded to C atoms have been omitted [symmetry code: (ii) $1 - x, 1 - y, 1 - z$].

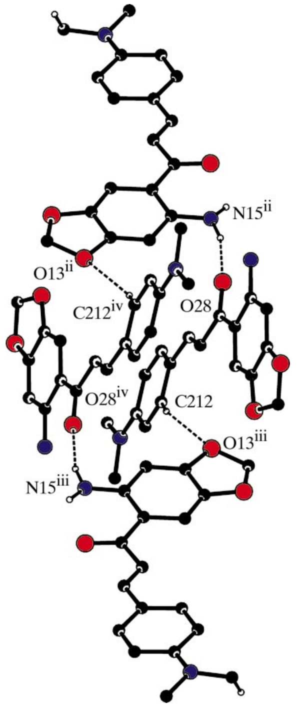

Figure 5
A view of the $R_4^4(26)$ rings which link the tetramers in (II) [symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, y, z - 1$; (iv) $1 - x, 1 - y, -z$]. For the sake of clarity, H atoms bonded to C or N atoms and not involved in this motif have been omitted, as has the unit-cell box.

(x, $y - 1$, z) is 3.445 Å (Fig. 6). It is worth noting that the dihedral angle between these planes, 3.50°, is in fact the dihedral angle between the two components of the benzo-1,3-dioxol-5-yl group, which is not in itself planar. There is no π–π stacking in (II).

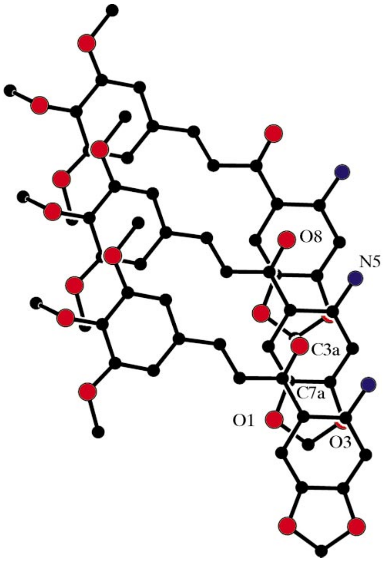

Figure 6
A view of the $\pi\cdots\pi$ stacking in (I). For the sake of clarity the unit-cell box has been omitted.

Experimental

For (I), a mixture of 6′-amino-3′,4′-(methylenedioxy)acetophenone (0.50 g, 2.79 mmol), 3,4,5-trimethoxybenzaldehyde (2.79 mmol), ethanol (10 ml) and NaOH (0.5 ml, 20% aq.) was heated to 333–343 K for 10–15 min and the reaction monitored by thin-layer chromatography. After cooling, the solid which formed was filtered off and washed with ethanol to yield pure (I) as orange crystals (93% yield; m.p. 464 K). For (II), a mixture of 6′-amino-3′,4′-(methylenedioxy)acetophenone (0.50 g, 2.79 mmol), 4-(*N*,*N*-dimethylamino)benzaldehyde (2.79 mmol), ethanol (10 ml) and NaOH (0.5 ml, 20% aq.) was heated to 333–343 K for 10–15 min and the reaction monitored by thin-layer chromatography. After cooling, the solid which formed was filtered off and washed with ethanol to yield pure (II) as purple crystals (46% yield; m.p. 435 K). For (I) and (II), crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared samples.

Compound (I)

Crystal data

$C_{19}H_{19}NO_6$
$M_r = 357.35$
Monoclinic, $P2_1/c$
$a = 23.5477$ (4) Å
$b = 4.9605$ (1) Å
$c = 14.2556$ (8) Å
$\beta = 100.702$ (1)°
$V = 1636.21$ (10) Å^3
$Z = 4$
$D_x = 1.451$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3622 reflections
$\theta = 3.1$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 150$ (1) K
Block, orange
0.4 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.958$, $T_{max} = 0.989$
11 152 measured reflections
3622 independent reflections
2832 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 27.5°$
$h = -30 \rightarrow 30$
$k = -6 \rightarrow 6$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.124$
$S = 1.03$
3622 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 0.3552P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N5—H5*A*⋯O8	0.88	2.01	2.651 (2)	129
C16—H16⋯O1^{i}	0.95	2.51	3.398 (2)	155

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

Compound (II)

Crystal data

$C_{18}H_{18}N_2O_3$
$M_r = 310.34$
Triclinic, $P\overline{1}$
$a = 9.5849$ (2) Å
$b = 12.3218$ (4) Å
$c = 13.3304$ (4) Å
$\alpha = 83.4617$ (14)°
$\beta = 80.2411$ (17)°
$\gamma = 85.7271$ (16)°
$V = 1539.04$ (8) Å^3
$Z = 4$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6884 reflections
$\theta = 3.1$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 150$ (1) K
Block, purple
0.22 × 0.14 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.980$, $T_{max} = 0.989$
23 078 measured reflections
6884 independent reflections
4873 reflections with $I > 2\sigma(I)$
$R_{int} = 0.085$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N15—H15*A*⋯O18	0.88	2.03	2.6433 (14)	125
N15—H15*B*⋯O28^{i}	0.88	2.26	3.0867 (13)	157
N25—H25*A*⋯O28	0.88	1.94	2.6237 (17)	133
N25—H25*B*⋯O18	0.88	2.20	3.0606 (17)	165
C14—H14⋯O28^{i}	0.95	2.38	3.2067 (18)	145
C24—H24⋯O18	0.95	2.52	3.3212 (19)	142
C212—H212⋯O13^{ii}	0.95	2.60	3.4508 (18)	149

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.154$
$S = 1.02$
6884 reflections
419 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

For both compounds, H atoms were treated as riding, with C—H = 0.95–0.99 Å. In the case of the N—H bonds, the H atoms were initially located on a difference Fourier map. The bond lengths were then *DFIX*ed (*SHELXL*97; Sheldrick, 1997) to 0.88 Å with an s.u. of 0.005 until a value close to 0.88 Å was obtained, at which stage they were *AFIX*ed (*SHELXL*97) and allowed to ride on their parent atoms.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1178). Services for accessing these data are described at the back of the journal.

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