

2'-Hydroxy-4''-dimethylamino-  
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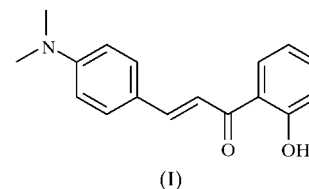
The title compound, 3-[4-(dimethylamino)phenyl]-1-(2-hydroxyphenyl)prop-2-en-1-one,  $C_{17}H_{17}NO_2$ , is a chalcone derivative substituted by 2'-hydroxyl and 4''-dimethylamino groups. The crystal structure indicates that the aniline and hydroxyphenyl groups are nearly coplanar, with a dihedral angle of  $10.32(16)^\circ$  between their phenyl rings. The molecular planarity of this substituted chalcone is strongly affected by the 2'-hydroxyl group.

## Comment

In the past decade, synthetic chemosensors have been the focus of research related to molecular opto-electronics. As a typical intramolecular charge-transfer (ICT) compound, 4''-dimethylaminochalcone (DMAC) has been reported to be a potential chemosensor due to its intense emission (DiCasare & Lakowicz, 2000). In particular, when it is substituted by different groups and/or is in different micro-surroundings, the fluorescent properties of the molecule can be significantly altered, due to the different ICT nature of the excited states. To understand this structure–property relationship, some interesting work has been carried out. Murafuji *et al.* (1999) have reported two crystal structures of similar compounds with different groups at the 2'-position, namely 2'-diethylboryl-4''-dimethylaminochalcone and DMAC. In the former structure, the dihedral angle between the phenyl rings is  $3.28(9)^\circ$ , but in the latter, which has no substituted group, the dihedral angle is  $18.5(2)^\circ$ . The difference comes from an extra intramolecular B–O coordination bond. In this paper, we report the structure of the title compound, (I), which is 2'-hydroxy-DMAC.

The molecule of (I), along with the atom-numbering scheme, is illustrated in Fig. 1. This molecule can be classified into the  $D-\pi-A$  (electron donor– $\pi$ -bridge–electron acceptor) model. The dimethylamino, the benzoyl and the styrene groups act as the electron donor, the electron acceptor and the  $\pi$  bridge, respectively. As expected, the backbone of the compound is nearly planar (Fig. 2). The dihedral angle

between the phenyl rings of the aniline and benzoyl groups is only  $10.32(16)^\circ$ . There is some noticeable conjugation in the  $C10-C9=C8-C7$  bridge between the two phenyl rings, as seen in the increased length of the  $C8=C9$  double bond [ $1.344(4) \text{ \AA}$ ] and the decreased length of the  $C7-C8$  [ $1.447(4) \text{ \AA}$ ] and  $C9-C10$  [ $1.431(4) \text{ \AA}$ ] single bonds.



Comparing our results with those of Murafuji *et al.* (1999), it can be seen that the planarity of the substituted chalcone molecule is strongly affected by the substituted group on the 2'-position. The hydroxyl group is connected to the carbonyl by an  $O1-H \cdots O2$  hydrogen bond (Table 1). This  $H \cdots O$  intramolecular interaction is obviously weaker than the  $O \rightarrow B$  coordination bond reported by Murafuji *et al.* (1999).

It is interesting to compare the origination of the dihedral angles of DMAC [ $18.5(2)^\circ$ ] and (I) [ $10.32(16)^\circ$ ]. In DMAC (with the same atom-numbering scheme as in Fig. 1), the  $C5-C4-C7-C8$  [ $20.3(5)^\circ$ ] and  $C3-C4-C7-O$  [ $19.0(5)^\circ$ ] torsion angles are remarkable, and make the twist between the carbonyl plane ( $C8-C7-O2$ ) and the phenyl plane ( $C1-C6$ ) the main contribution to the non-planarity of DMAC. In (I), however, the carbonyl plane ( $C8-C7-O2$ ) and the phenyl plane ( $C1-C6$ ) are nearly coplanar. Obviously, the torsion to

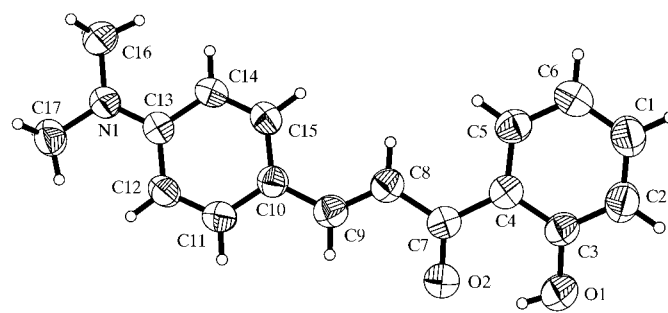


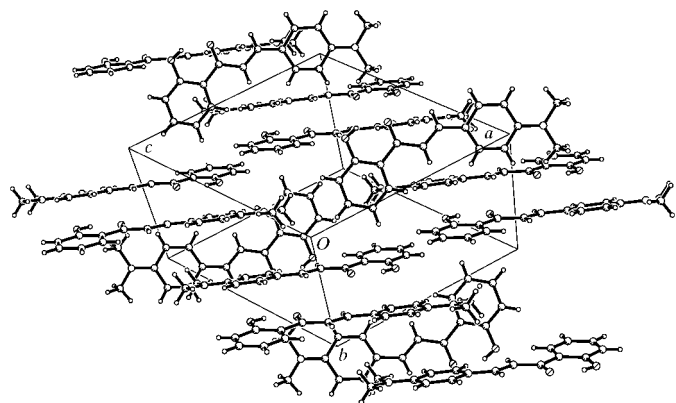
Figure 1

A view of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

make the carbonyl plane parallel to the phenol plane is the  $O1-H \cdots O2$  intramolecular interaction. This seems to mean that the bonding between the substituted group at the 2'-position and the O atom of the carbonyl is helpful for enhancing the planarity of the whole molecule. The stronger the bonding, the better the planarity. From this point of view, we can understand why the planarity of 2'-hydroxy-DMAC, (I), is better than DMAC but poorer than 2'-diethylboryl-DMAC. The dihedral angle between the two phenyl rings in (I) comes from a gradual small skewing of the carbon chain between the two phenyl rings, and the  $C7-C8=C9-C10$  torsion angle of  $3.9(3)^\circ$  is the largest in this skewing series.

As shown in Fig. 2, the molecular planes of all the molecules are either perpendicular or parallel to each other in the crystal. Each pair of two nearest molecules is coupled in a head-to-tail manner. Thus, the main intermolecular interaction can be supposed to be dipole–dipole interactions. From a check of the intermolecular atomic distances, there are no other obvious short intermolecular contacts in the crystal.

Concerning the structure–property relationship, we have measured the fluorescent properties of both DMAC and 2'-hydroxy-DMAC, (I), using an Edinburgh FLS920 spectrometer. Both compounds have the same peak position in their emission spectra, but the fluorescent intensity and quantum



**Figure 2**  
A packing diagram for (I).

yield of the former are about 100 times higher than that of the latter in four kinds of solvent with different polarity, from toluene to MeCN. We think that the O1–H···O2 hydrogen bond has both a positive and a negative influence on the emission properties. The planarity and invariability of a  $\pi$ -conjugated organic molecule are important for fluorescence. The intramolecular hydrogen bond in (I) is helpful for enhancing the molecular planarity, but is not useful for enhancing the molecular invariability (this hydrogen bond may induce some structural variability by potentially inducing more resonance structures). The combined effect is the enhanced non-radiative energy transfer of (I) and therefore the enhanced fluorescence quenching.

## Experimental

A mixture of 2'-hydroxyacetophenone (2.72 g) and boron trifluoride etherate (2.6 ml, 48%  $\text{BF}_3$ ) was heated to reflux for 1 h under an  $\text{N}_2$  atmosphere. 4-Dimethylaminobenzaldehyde (3.0 g) in acetic anhydride (10 ml) was then added dropwise. The temperature was kept at 363 K for a further 2 h. The mixture was then added dropwise to water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was separated out and further purified by column chromatography using petroleum ether–chloroform (1:1) as eluant. After removal of the solvent under reduced pressure, dark-red microcrystals of (I) were obtained (yield 78%, 4.15 g; m.p. 449–450 K). A sample of (I) for structure determination was obtained by recrystallization from acetonitrile.

## Crystal data

$\text{C}_{17}\text{H}_{17}\text{NO}_2$   
 $M_r = 267.32$   
Monoclinic,  $P2_1/c$   
 $a = 12.1194$  (14) Å  
 $b = 10.2869$  (8) Å  
 $c = 12.5048$  (16) Å  
 $\beta = 115.864$  (8)°  
 $V = 1402.8$  (3) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.266$  Mg m<sup>−3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 40 reflections  
 $\theta = 5.1$ – $12.8^\circ$   
 $\mu = 0.08$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
Prism, red  
 $0.36 \times 0.30 \times 0.20$  mm

## Data collection

Bruker P4 diffractometer  
 $\omega$  scans  
Absorption correction:  $\psi$  scan  
(XSCANS; Siemens, 1996)  
 $T_{\min} = 0.807$ ,  $T_{\max} = 0.984$   
3510 measured reflections  
2745 independent reflections  
1353 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$   
 $\theta_{\max} = 26^\circ$   
 $h = -14 \rightarrow 1$   
 $k = -1 \rightarrow 12$   
 $l = -14 \rightarrow 15$   
3 standard reflections  
every 97 reflections  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.065$   
 $wR(F^2) = 0.216$   
 $S = 1.01$   
2745 reflections  
182 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1111P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.32$  e Å<sup>−3</sup>  
 $\Delta\rho_{\min} = -0.22$  e Å<sup>−3</sup>  
Extinction correction: SHELXL97  
Extinction coefficient: 0.012 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1A···O2	0.82	1.77	2.504 (3)	147

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms, with  $\text{C–H} = 0.93$ – $0.96$  Å and  $\text{O–H} = 0.82$  Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1067). Services for accessing these data are described at the back of the journal.

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