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4-[3-(3,4-Dimethoxyphenyl)prop-2-enoyl]phenyl methacrylate and 4-[3-(2-bromophenyl)prop-2-enoyl]-phenyl methacrylate

A. Jeyabharathi,[a] M. N. Ponnuswamy,[a] S. Nanjundan,[b] Hoong-Kun Fun,[c]* Suchada Chantrapromma,[c]† Anwar Usman[c] and Ibrahim Abdul Razak[c]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, [b]Department of Chemistry, Anna University, Chennai 600 025, India, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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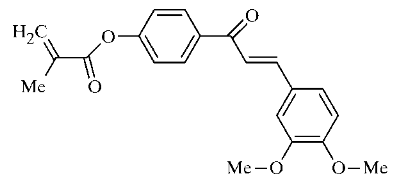
Chalcones (α,β-unsaturated ketones) are effective antitumour agents. It has been proved that having halogen or methoxy groups substituted in various positions of the phenyl ring enhances the activity of chalcones many times. The title compounds, $C_{21}H_{20}O_5$ and $C_{19}H_{15}BrO_3$, respectively, were chosen for crystallographic study in order to determine their structures and conformations. In both compounds, the keto group is in the *s-cis* conformation and is almost planar. There are weak intramolecular interactions in both structures.

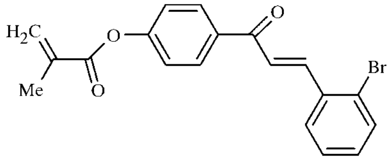
Comment

Chalcones possess multi-protecting, biochemical, antifungal, antimalarial and antifertility activities. The carbonyl group is a characteristic functional group in chalcones. In recent years, the synthesis of polymers having a photosensitive functional group has been an active field of research in polymer science. Monomers having structures similar to the title compounds, 4-[3-(3,4-dimethoxyphenyl)prop-2-enoyl]phenyl methacrylate, (I), and 4-[3-(2-bromophenyl)prop-2-enoyl]phenyl methacrylate, (II), have been polymerized in solution using free-radical initiators (Balaji *et al.*, 2000; Subramanian *et al.*, 2001). These polymers, containing an α,β-unsaturated carbonyl group, undergo crosslinking upon irradiation with UV light or an electron beam and are being used as photoresistors (Hyder Ali & Srinivasan, 1997; Rehab & Salahuddin, 1999). These photosensitive polymers find application in the fields of integrated circuit technology, printing technology and photocurable coatings (Nagamatzu & Inui, 1977).

The keto group is in the *s-cis* conformation in compounds (I) and (II), as can be seen from the C7—C8—C9—O1 torsion-angle values of 4.7 (3)° for (I) and 7.2 (6)° for (II). The two phenyl rings make dihedral angles with the keto group of 8.5 (2) and 11.8 (1)° for (I), and 4.8 (2) and 7.6 (2)° for (II). In general, the bond lengths in these conjugated systems are longer than the double bonds and shorter than the single bonds. In both structures, the bond lengths agree with reported values (Carpy *et al.*, 1978). From the torsion angle values C5—C4—C7—C8 = −176.0 (2)°, C4—C7—C8—C9 = 177.5 (2)°, C7—C8—C9—C10 = −173.2 (2)° and C8—C9—C10—C15 = −167.2 (2)° in (I), and C1—C6—C7—C8 = 170.6 (4)°, C6—C7—C8—C9 = 178.9 (3)°, C7—C8—C9—C10 = −173.8 (4)° and C8—C9—C10—C11 = 8.1 (6)° in (II), it is clear that the unsaturated ketone system is not strictly planar. This deviation from planarity affects the π-electron conjugation. The H atoms at C7 and C8 are *trans*. The opening of the C4—C7—C8 angle to 129.5 (2)° in (I) and the C6—



(I)



(II)

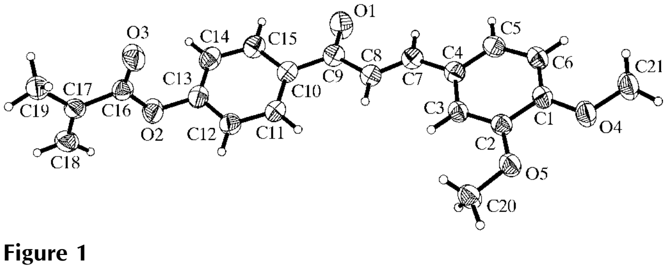


Figure 1
The molecular structure of compound (I) drawn with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

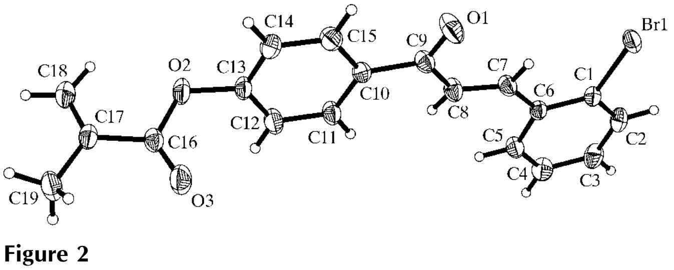


Figure 2
The molecular structure of compound (II) drawn with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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† Permanent address: Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

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C7—C8 angle to 127.3 (4)° in (II) can be ascribed to the short interatomic non-bonded interaction between atoms H8 and H3 in (I), which are separated by a distance of 2.309 (2) Å, and the interaction between atoms H5 and H8 in (II), which are separated by a distance of 2.211 (1) Å (Tokuno *et al.*, 1986). This non-bonded interaction also produces an appreciable twist about the C4—C7 bond for (I) and the C6—C7 bond for (II), at the expense of the conjugation energy of the system. The exocyclic angles about C10 reveal deviations from normal trigonal values, with a larger C9—C10—C11 angle [124.1 (2)° for (I) and 123.5 (3)° for (II)] and a smaller C9—C10—C15 angle [117.6 (2)° for (I) and 118.1 (3)° for (II)]. There are two weak C—H···O intramolecular interactions in (I) and (II), and one weak C—H···Br interaction in (II) (Tables 2 and 4).

Displacement-ellipsoid plots of the molecules of (I) and (II) are shown in Figs. 1 and 2, respectively. Figs. 3 and 4 show the packing of molecules of (I) and (II), viewed down the *a* axis in each case.

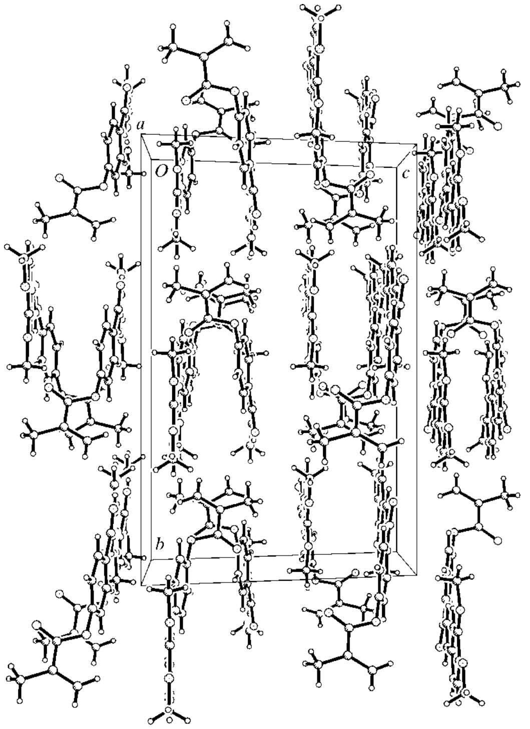

Figure 3
Packing diagram of (I) viewed down the *a* axis.

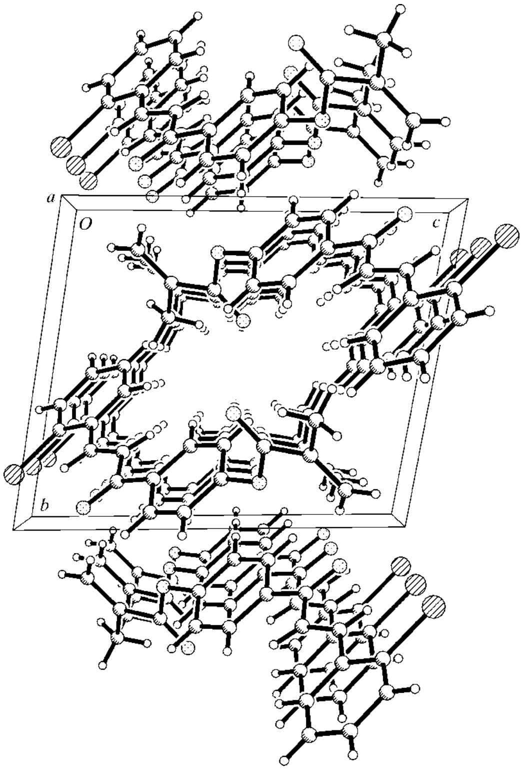

Figure 4
Packing diagram of (II) viewed down the *a* axis.

Experimental

The syntheses of compounds (I) and (II) consist of two steps. 3,4-Dimethoxystyryl 4-hydroxyphenyl ketone and 1-bromostyryl 4-hydroxyphenyl ketone were prepared by the Claissen–Schmidt condensation of 3,4-dimethoxybenzaldehyde or 1-bromobenzaldehyde with 4-hydroxyacetophenone in aqueous alcohol. Compounds (I) and (II) were then prepared by reacting 3,4-dimethoxystyryl 4′-hydroxyphenyl ketone or 1-bromostyryl 4′-hydroxyphenyl ketone in methyl ethyl ketone with methacryloyl chloride in the presence of triethylamine.

Compound (I)

Crystal data

$C_{21}H_{20}O_5$
$M_r = 352.37$
Monoclinic, $C2/c$
$a = 13.381$ (2) Å
$b = 20.813$ (2) Å
$c = 13.881$ (2) Å
$\beta = 109.68$ (1)°
$V = 3640.0$ (8) Å^3
$Z = 8$

$D_x = 1.286$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.1$–25.0°
$\mu = 0.75$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3812 measured reflections
3549 independent reflections
2444 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\rm max} = 72.0°$

$h = -2 \rightarrow 16$
$k = 0 \rightarrow 25$
$l = -17 \rightarrow 16$
3 standard reflections every 200 reflections frequency: 120 min intensity decay: <0.1%

Table 1
Selected geometric parameters (Å, °) for (I).

C1—O4	1.362 (3)	C9—C8	1.475 (3)
O5—C2	1.363 (2)	O2—C16	1.344 (3)
O5—C20	1.413 (2)	O2—C13	1.408 (3)
O4—C21	1.426 (3)	C16—O3	1.197 (2)
C9—O1	1.231 (2)		
O4—C1—C6	124.93 (18)	O5—C2—C3	125.13 (17)
O4—C1—C2	115.32 (18)	O5—C2—C1	114.99 (17)
C11—C10—C9	124.07 (18)	C8—C7—C4	129.5 (2)
C15—C10—C9	117.59 (19)		
C15—C10—C9—C8	167.17 (19)	C9—C8—C7—C4	177.5 (2)
O1—C9—C8—C7	4.7 (3)	C5—C4—C7—C8	−176.0 (2)
C10—C9—C8—C7	−173.18 (19)		

Table 2
Short-contact geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7$\cdots$O1	0.93	2.42	2.784 (3)	103
C18—H18$B\cdots$O2	0.93	2.34	2.685 (3)	101

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.163$
$S = 1.04$
3549 reflections
238 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 0.6924P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Compound (II)

Crystal data

$C_{19}H_{15}BrO_3$
$M_r = 371.22$
Triclinic, $P\overline{1}$
$a = 7.5272$ (3) Å
$b = 10.1940$ (4) Å
$c = 11.5780$ (4) Å
$\alpha = 96.227$ (1)°
$\beta = 98.428$ (1)°
$\gamma = 108.763$ (1)°
$V = 820.54$ (5) Å^3

$Z = 2$
$D_x = 1.502$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4174 reflections
$\theta = 1.8$–29.5°
$\mu = 2.52$ mm^{-1}
$T = 293$ (2) K
Block, light yellow
0.44 × 0.32 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.404$, $T_{\max} = 0.752$
4721 measured reflections

2840 independent reflections
2355 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 8$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.146$
$S = 0.99$
2840 reflections
209 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Br1—C1	1.903 (4)	O2—C13	1.410 (5)
O1—C9	1.207 (5)	O3—C16	1.199 (5)
O2—C16	1.359 (5)	C7—C8	1.320 (5)
C11—C10—C9	123.6 (3)	C15—C10—C9	118.2 (4)
C1—C6—C7—C8	170.6 (4)	C7—C8—C9—C10	−173.8 (4)
C6—C7—C8—C9	178.9 (3)	C8—C9—C10—C11	8.1 (6)
C7—C8—C9—O1	7.2 (6)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7$A\cdots$Br1	0.93	2.71	3.175 (4)	112
C7—H7$A\cdots$O1	0.93	2.44	2.781 (5)	101
C18—H18$C\cdots$O2	0.93	2.37	2.700 (6)	100

After checking their presence in a difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms (C—H = 0.93 and 0.96 Å).

For compound (I), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1978); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

For compound (II), data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1204). Services for accessing these data are described at the back of the journal.

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