organic papers

Chalcone and its hydroxobromo derivative: a 1:1 mixed crystal containing chalcone and 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]propan-1-one

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In the structure of a mixed crystal, $C_{17}H_{17}BrO_2S\cdot C_{17}H_{16}OS$, containing chalcone and 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]propan-1-one, the two molecules are linked by a strong hydrogen bond between the alcohol H atom of 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]propan-1-one and the ketone group of chalcone.

Comment

There is currently great demand for large and high quality ferroelectric or piezoelectric single crystals with minimum defects and inhomogenities. An important goal of crystal growth is the improvement of microscopic and macroscopic homogeneity, which is a necessity for any application. Different types of crystals being used are semiconductor crystals, oxide crystals, alkali halide crystals and non-linear optical (NLO) crystals. The NLO effect in organic compounds originates from a strong donor–acceptor intermolecular interaction, a delocalized π-electron system and the ability to crystallize in a non-centrosymmetric structure. Among several organic compounds reported for their NLO properties, chalcone derivatives are prominent materials for their excellent blue light transmittance and good crystallizability. They provide the configuration necessary to show NLO activity, with two planar rings connected through a conjugated double bond (Goto *et al.*, 1991; Uchida *et al.*, 1998; Tam *et al.*, 1989; Indira *et al.*, 2002). From a search of noncentrosymmetric chalcone derivatives in the Cambridge Structural Database (*ConQuest* Version 1.8; Allen, 2002), it seems that a necessary but not sufficient condition (Teh *et al.*, 2006) is substitution on either of the phenyl rings in the *para* position (Rabinovich, 1970; Arai *et al.*, 1994; Rabinovich & Shakked, 1974; Ravishankar *et al.*, 2005; Rabinovich & Schmidt, 1970; Li *et al.*, 1992; Gupta *et al.*, 2002; Turowska-Tyrk *et al.*, 2003; Zheng *et al.*, 1992; Patil *et al.*, 2006). It is speculated that, in order to improve the activity, more bulky substituents should be introduced to increase the spontaneous polarization of a noncentrosymmetric crystal structure (Fichou *et al.*, 1988). The molecular hyperpolarizability, β, is strongly influenced not only by the electronic effect but also by the steric effect of the substituents (Cho *et al.*, 1996).

In a continuation of our quest to synthesize new materials which could find use in the photonics industry, we have synthesized a new chalcone. However, chalcone derivatives often have low melting points, which can be a drawback for the application of these crystals in optical instruments. Chalcone dibromides usually have higher melting points and are thermally stable. With this in mind, we wanted to prepare a new dibromochalcone starting from 1-(4-methylphenyl)-3-[4-

(methylsulfanyl)phenyl]prop-2-en-1-one in chloroform using commercial-grade bromine. However, single-crystal X-ray analysis revealed that compound (I) is a mixed crystal of
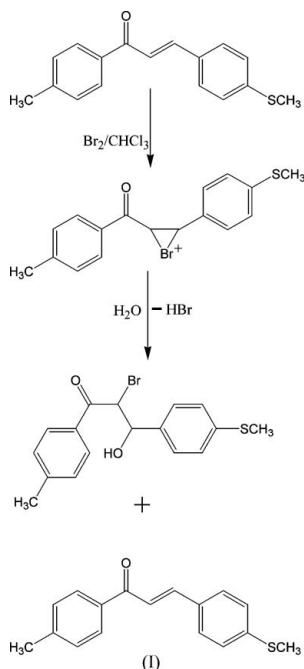
chalcone and 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]propan-1-one, as the bromination reaction is incomplete. The hydroxobromo derivative of chalcone is formed by the cleavage of a cyclic bromonium intermediate by nucleophilic attack of water on the bromonium ion instead of on the bromide ion (see scheme). Thus, some of the chalcone remains unreacted, giving a mixed crystal with 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]propan-1-one linked by hydrogen bonding. Bromination was carried out in commercial-grade
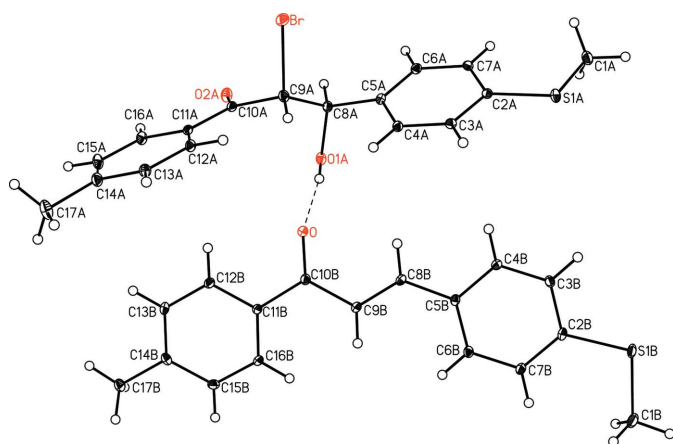
Figure 1
A view showing the two components of (I), linked by a strong hydrogen bond (dashed line) between the alcohol H atom of 2-bromo-3-hydroxy-1-(4-methylphenyl)-3-[4-(methylthio)phenyl]propan-1-one and the ketone group of chalcone. Displacement ellipsoids are drawn at the 20% probability level.
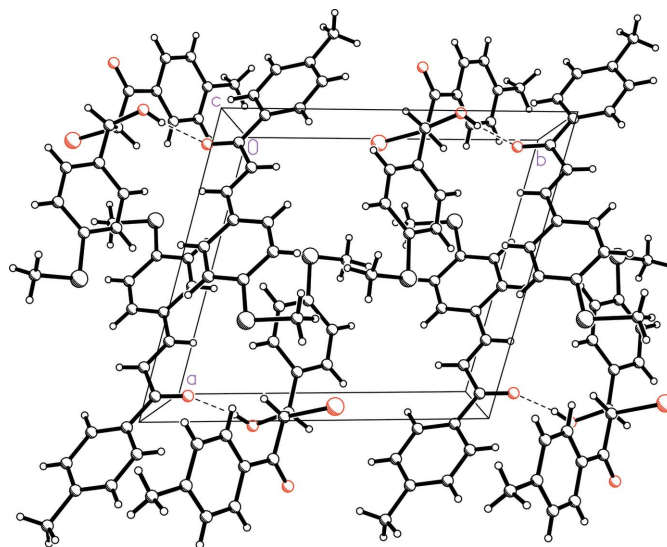
Figure 2
The molecular packing, viewed down the c axis. Hydrogen bonds are shown as dashed lines

bromine in chloroform, and moisture was not excluded. The reduction of the double bond in the chalcone derivative is confirmed by the structural results, which show the addition of an –OH function to C8A, and by the lengthening of the C8—C9 bond from 1.344 (3) for C8B—C9B to 1.505 (3) Å for C8A—C9A and the change in the angles about C8A and C9A from trigonal (sp^2) to tetrahedral (sp^3) values.

Experimental

To a solution of 1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one (2.68 g, 0.01 mol) in chloroform (50 ml), bromine (1.60 g, 0.01 mol) in chloroform (20 ml) was added slowly with stirring. After the completion of the addition of the bromine solution, the reaction mixture was stirred for 24 h. Excess chloroform was distilled off under reduced pressure. The solid obtained was dried and recrystallized from acetone.

Crystal data

$C_{17}H_{17}BrO_2S \cdot C_{17}H_{16}OS$	$V = 1500.5$ (4) Å^3
$M_r = 633.63$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.402$ Mg m^{-3}
$a = 10.5026$ (15) Å	Mo $K\alpha$ radiation
$b = 11.4926$ (17) Å	$\mu = 1.54$ mm^{-1}
$c = 13.1326$ (19) Å	$T = 446$ (2) K
$\alpha = 97.173$ (3)°	Chunk, colourless
$\beta = 98.157$ (2)°	$0.50 \times 0.40 \times 0.35$ mm
$\gamma = 104.125$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	26944 measured reflections
φ and ω scans	7025 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5636 reflections with $I > 2\sigma(I)$
$T_{min} = 0.774$, $T_{max} = 1.000$	$R_{int} = 0.070$
(expected range = 0.451–0.583)	$\theta_{max} = 27.9°$

Refinement on F^2		H atoms treated by a mixture of	
$R[F^2 > 2\sigma(F^2)] = 0.040$		independent and constrained	
$wR(F^2) = 0.115$		refinement	
$S = 1.06$		$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2]$	
7025 reflections		where $P = (F_o^2 + 2F_c^2)/3$	
366 parameters		$(\Delta/\sigma)_{max} = 0.001$	
		$\Delta\rho_{max} = 0.84$ e Å^{-3}	
		$\Delta\rho_{min} = -0.62$ e Å^{-3}	

Table 1
Selected geometric parameters (Å, °).

Br—C9A	1.978 (2)	C5A—C8A	1.511 (3)
S1A—C2A	1.762 (2)	C8A—C9A	1.505 (3)
S1A—C1A	1.802 (2)	C9A—C10A	1.520 (3)
S1B—C2B	1.762 (2)	C10A—C11A	1.490 (3)
S1B—C1B	1.796 (3)	C5B—C8B	1.459 (3)
O—C10B	1.236 (3)	C8B—C9B	1.344 (3)
O1A—C8A	1.478 (3)	C9B—C10B	1.477 (3)
O2A—C10A	1.225 (3)	C10B—C11B	1.492 (3)
O1A—C8A—C9A	106.17 (17)	C6B—C5B—C4B	118.2 (2)
O1A—C8A—C5A	110.92 (18)	C6B—C5B—C8B	123.9 (2)
C9A—C8A—C5A	113.62 (19)	C4B—C5B—C8B	118.0 (2)
C8A—C9A—C10A	112.66 (19)	C9B—C8B—C5B	128.1 (2)
C8A—C9A—Br	109.50 (15)	C8B—C9B—C10B	119.8 (2)
C10A—C9A—Br	105.16 (15)	O—C10B—C9B	120.9 (2)
O2A—C10A—C11A	121.2 (2)	O—C10B—C11B	119.5 (2)
O2A—C10A—C9A	119.5 (2)	C9B—C10B—C11B	119.67 (19)
C11A—C10A—C9A	119.30 (19)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1A—H1A$\cdots$O	0.82	1.95	2.760 (2)	170

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. The H attached to O1A was located in a difference Fourier map and idealized with O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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