Topochemistry. Part XXXIV.[1] Crystal and Molecular Structure of *p'*-Bromochalcone

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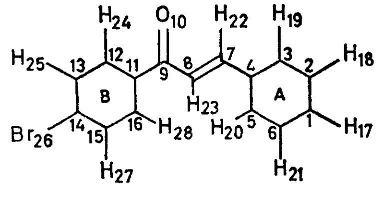
The crystal structure of *p'*-bromochalcone has been solved from partial three-dimensional photographic data by the heavy-atom technique, and refined by a least-squares programme to R' 0·03 and R 0·08. Crystals are monoclinic, space group $P2_1/c$ with $Z = 8$ in a unit cell of dimensions: $a = 15{\cdot}10(1)$, $b = 5{\cdot}90(1)$, $c = 31{\cdot}13(2)$ Å, $\beta = 108{\cdot}6(1)°$.

Bond lengths and angles in the two molecules of the asymmetric unit, which agree within their estimated standard deviations of 0·02 Å and 1·0°, are similar to those observed in other chalcones. Both molecules are non-planar, the angles between the planes of the two phenyl groups being 50°.

The molecules pack in stacks along [010] with the bromine atoms spiralling along the 2_1 axes.

THE structure analysis of *p'*-bromochalcone has been undertaken as part of our studies on the correlation between molecular packing modes, molecular conformation, and solid-state photochemical reactivity.



p'-Bromochalcone (I). Numbering of atoms used in the analysis of chalcone derivatives

EXPERIMENTAL

The compound was prepared by the condensation of benzaldehyde and *p'*-bromoacetophenone in alcoholic sodium hydroxide.[2] Crystals grown (m.p. 104—105 °C) from slowly cooled solutions in methylcyclohexane are monoclinic plates elongaged along [010], showing {001} and {20$\bar{1}$}. Cell constants were determined from Weissenberg and precession photographs.

Crystal Data.—$C_{15}H_{11}BrO$, $M = 287{\cdot}1$, $a = 15{\cdot}10(1)$, $b = 5{\cdot}90(1)$, $c = 31{\cdot}13(2)$ Å, $\beta = 108{\cdot}6(1)$, $U = 2628{\cdot}1$ Å^3, $D_m = 1{\cdot}44$, $Z = 8$, $D_c = 1{\cdot}45$, $F(000) = 1152$. Space group $P2_1/c$ from systematic absences: $h0l$ for l odd and $0k0$ for k odd. Cu-K_α radiation $\lambda = 1{\cdot}4518$ Å; μ(Cu-K_α) = 45·1 cm^{-1}.

A crystal mounted along [010], of dimensions 0·09 × 0·20 × 1·10 mm was used to record the intensities of the layers $h0$—$4l$ by the multiple-film equi-inclination Weissenberg technique; intensities were estimated visually. Data processing included absorption correction [3] and spotshape correction [4] for upper levels.

The [010] projection was solved by means of a sharpened Patterson synthesis $^sP(xz)$, [with coefficients $F^2(h0l)/f^2$ where $f = f_{Br} \exp(-4{\cdot}8 \sin^2 \theta/\lambda^2)$] which revealed the co-ordinates of the two bromine atoms; these were used to determine the signs of $F(h0l)$. Since the contributions of the bromine atoms to the largest structure factors, $F(40\bar{4})$ and $F(40\bar{2})$, were negligible Fourier maps were computed with the four sign-permutations of these two reflections; a molecular model could be fitted to one map only. The x, z co-ordinates of the carbon and oxygen atoms thus determined were refined in a full-matrix least-squares programme together with anisotropic thermal parameters for bromine and isotropic parameters for all other atoms. Agreement factors at this stage were R 0·08 and R' 0·04 [$R' = \Sigma w(k^2F_o{}^2 - |F_c|^2)^2/\Sigma wk^4F_o{}^4$].

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TABLE 1

Atomic co-ordinates (fractional $\times 10^4$ for C, H, and O; $\times 10^5$ for Br) and standard deviations referred to axes *a*, *b*, *c*

	Molecule (1)			Molecule (2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(1)	2549(8)	−290(21)	6915(3)	5098(8)	4686(21)	7001(4)
C(2)	2132(8)	1823(21)	6934(3)	5530(7)	6783(21)	7000(3)
C(3)	1817(6)	3164(15)	6548(3)	5343(6)	8058(15)	6612(3)
C(4)	1909(6)	2376(16)	6140(3)	4718(6)	7277(17)	6202(3)
C(5)	2297(7)	225(17)	6121(3)	4300(7)	5126(19)	6195(3)
C(6)	2639(7)	−1070(16)	6517(4)	4489(7)	3831(18)	6594(4)
C(7)	1592(6)	3864(15)	5749(3)	4480(6)	8699(15)	5797(3)
C(8)	1475(7)	3340(16)	5316(3)	4011(7)	8141(16)	5373(3)
C(9)	1213(7)	5119(22)	4962(3)	3787(7)	9954(21)	5026(3)
O(10)	1270(5)	7161(13)	5054(2)	3870(6)	12016(13)	5125(2)
C(11)	899(6)	4340(16)	4481(3)	3433(6)	9278(17)	4535(3)
C(12)	1023(6)	5867(16)	4154(3)	2901(6)	10863(16)	4225(3)
C(13)	716(6)	5230(18)	3700(3)	2578(7)	10313(19)	3771(3)
C(14)	306(6)	3108(18)	3584(3)	2809(7)	8203(18)	3637(3)
C(15)	161(7)	1622(15)	3889(3)	3351(7)	6645(16)	3933(3)
C(16)	483(7)	2205(15)	4340(3)	3661(6)	7168(16)	4396(3)
H(17)	2798	−1327	7177	5237	3767	7297
H(18)	2054	2402	7227	5932	7479	7265
H(19)	1525	4689	6564	5669	9498	6632
H(20)	2330	−390	5824	3850	4466	5900
H(21)	2944	−2534	6518	4192	2303	6590
H(22)	1444	5459	5811	4699	10306	5847
H(23)	1564	1748	5231	3809	6495	5288
H(24)	1332	7418	4245	2751	12398	4329
H(25)	790	6295	3458	2180	11434	3541
Br(26)	−689(9)	23276(23)	29605(3)	23617(9)	74980(23)	30117(3)
H(27)	−174	140	3784	3528	5149	3813
H(28)	416	1092	4562	4048	6027	4629

TABLE 2

Equations of best planes (in fractional co-ordinates) and relevant distances (Å) from planes

Atom	Molecule (1)	Molecule (2)
	Ring A	
	$-13{\cdot}202x - 2{\cdot}559y + 2{\cdot}231z + 1{\cdot}745 = 0$	$-13{\cdot}184x + 2{\cdot}606y + 14{\cdot}750z - 4{\cdot}812 = 0$
*C(1)	−0·003	0·014
*C(2)	0·011	−0·010
*C(3)	−0·003	−0·004
*C(4)	−0·013	0·012
*C(5)	0·013	−0·008
*C(6)	−0·011	−0·006
C(7)	−0·063	0·100
	Ring B	
	$13{\cdot}733x - 2{\cdot}378y - 5{\cdot}980z + 2{\cdot}472 = 0$	$13{\cdot}791x + 2{\cdot}314y - 12{\cdot}313z - 1{\cdot}302 = 0$
C(9)	−0·047	0·035
*C(11)	−0·005	−0·005
*C(12)	−0·002	0·010
*C(13)	−0·001	−0·003
*C(14)	0·010	−0·008
*C(15)	−0·018	0·014
*C(16)	0·016	−0·007
Br(26)	0·053	−0·018
	1,3-enone system	
	$14{\cdot}975x + 0{\cdot}308y - 6{\cdot}337z + 1{\cdot}112 = 0$	$14{\cdot}906x - 0{\cdot}314y - 14{\cdot}250z + 1{\cdot}882 = 0$
C(4)	0·153	−0·152
*C(7)	−0·028	0·026
*C(8)	0·055	−0·051
*C(9)	−0·058	0·052
*O(10)	0·032	−0·030
C(11)	−0·248	0·246

* Atoms used in the determination of best planes.

A three-dimensional sharpened Patterson line-synthesis yielded approximate y co-ordinates of bromine atoms of ($\frac{1}{4}$) and ($\frac{3}{4}$); in view of the pseudo-special positions of the bromine atoms electron-density maps based on bromine contribution were likely to be not sufficiently informative; instead, the y co-ordinates of the carbon and oxygen atoms were determined from the Br · · · C and Br · · · O vectors whose corresponding peaks were found on the Patterson line-syntheses ${}^{s}P(x_i y z_i)$. Next, the three-dimensional structure was refined by means of a block-diagonal least-squares procedure (one block per molecule) with anisotropic thermal parameters for the bromine, carbon, and oxygen atoms. Fixed hydrogen atoms were introduced; after several refinement cycles the agreement factors were reduced to R' 0·04 and R 0·10.

Comparison of F_o and F_c at this stage showed that for a large number of reflections, mainly those for which the absorption correction was large, F_o was appreciably larger than F_c. The cause of this is probably due to the large variations in the spot-area of the reflections, owing to the large thickness to breadth ratio of the crystal used. A quantitative analysis of this effect shows that an absorption correction would in fact enhance it. Refinement was accordingly continued with data uncorrected for absorption. The match between F_o and F_c was now slightly better; final agreement factors were R' 0·03; R 0·08. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20466 (40 pp., 1 microfiche).* The scattering-factor curves used for carbon and oxygen were taken from ref. 5, for hydrogen from ref. 6, and for bromine from ref. 7.

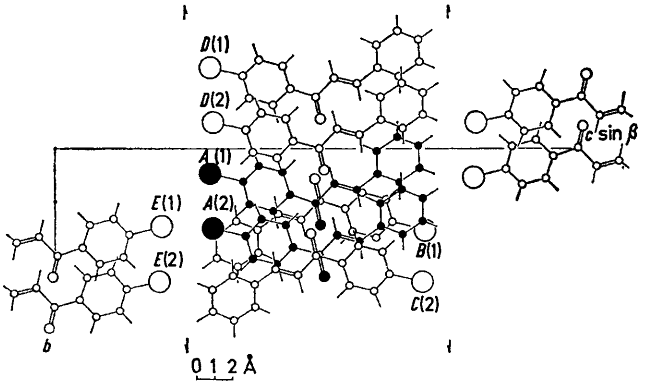

FIGURE 1

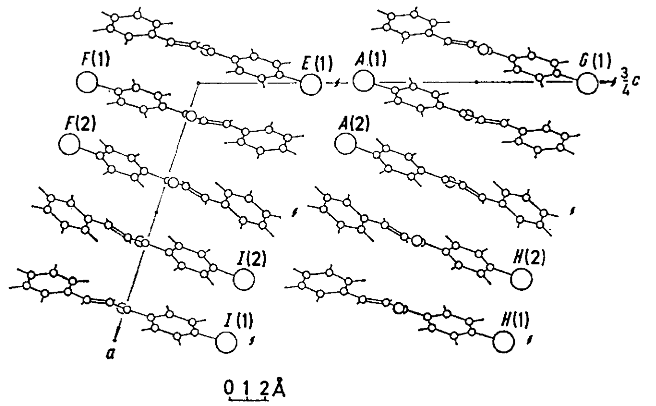

FIGURE 2

Standard deviations of all parameters were estimated by the usual least-squares formula [8] [$n = (2298 + 37 = 2335)$, $s = 307$].

RESULTS

Table 1 lists the fractional co-ordinates, together with their estimated standard deviations of all atoms in the two molecules in the asymmetric unit, referred to the unit-cell axes. The σ values in the positional parameters are nearly isotropic and average to 0·001, 0·010, and 0·008 Å for bromine, carbon, and oxygen atoms.

TABLE 3

Bond lengths (Å) and standard deviations

	Molecule (1)	Molecule (2)
C(1)–C(2)	1·406(18)	1·399(18)
C(2)–C(3)	1·389(14)	1·374(14)
C(3)–C(4)	1·401(14)	1·402(11)
C(4)–C(5)	1·407(15)	1·414(15)
C(5)–C(6)	1·401(13)	1·409(16)
C(6)–C(1)	1·370(16)	1·399(14)
C(4)–C(7)	1·453(12)	1·459(13)
C(7)–C(8)	1·337(14)	1·327(13)
C(8)–C(9)	1·483(15)	1·479(15)
C(9)–O(10)	1·235(15)	1·251(14)
C(9)–C(11)	1·490(13)	1·505(13)
C(11)–C(12)	1·415(14)	1·399(13)
C(12)–C(13)	1·392(13)	1·380(13)
C(13)–C(14)	1·392(14)	1·392(16)
C(14)–C(15)	1·359(14)	1·373(13)
C(15)–C(16)	1·375(12)	1·399(13)
C(16)–C(11)	1·414(17)	1·396(14)
C(14)–Br(26)	1·898(9)	1·892(9)

TABLE 4

Bond angles (°) and standard deviations

	Molecule (1)	Molecule (2)
C(6)–C(1)–C(2)	120·7(9)	119·4(10)
C(1)–C(2)–C(3)	120·3(10)	121·2(9)
C(2)–C(3)–C(4)	119·3(9)	120·8(9)
C(3)–C(4)–C(5)	120·1(8)	118·5(8)
C(4)–C(5)–C(6)	119·8(9)	120·6(8)
C(5)–C(6)–C(1)	119·8(10)	119·5(10)
C(3)–C(4)–C(7)	117·3(9)	120·4(9)
C(5)–C(4)–C(7)	122·7(9)	121·1(7)
C(4)–C(7)–C(8)	127·4(9)	128·6(9)
C(7)–C(8)–C(9)	120·3(9)	118·2(9)
C(8)–C(9)–O(10)	122·3(9)	122·9(9)
C(8)–C(9)–C(11)	116·9(10)	118·3(10)
O(10)–C(9)–C(11)	120·8(10)	118·8(9)
C(9)–C(11)–C(12)	116·9(9)	117·6(9)
C(9)–C(11)–C(16)	123·7(9)	120·5(8)
C(16)–C(11)–C(12)	119·4(8)	121·8(8)
C(11)–C(12)–C(13)	118·8(9)	119·1(9)
C(12)–C(13)–C(14)	118·8(9)	118·5(9)
C(13)–C(14)–C(15)	123·8(8)	123·4(8)
C(14)–C(15)–C(16)	117·9(8)	118·4(9)
C(15)–C(16)–C(11)	121·2(9)	118·7(8)
C(13)–C(14)–Br(26)	116·5(7)	117·6(7)
C(15)–C(14)–Br(26)	119·7(7)	119·0(8)

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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TABLE 5

Intermolecular contact distances (Å) between pairs of molecules identified by letters as in Figures 1 and 2. The fractional co-ordinates of the atoms in the two molecules A(1) and A(2) in the asymmetric unit are x_1, y_1, z_1, and x_2, y_2, z_2 respectively

All symmetry independent Br ··· Br and Br ··· C distances <3·8 Å, Br ··· H <3·4 Å, C ··· C <3·6 Å, C ··· H <3·2 Å and O ··· H and H ··· H <3·0 Å are listed. There are no Br ··· O distances <5·0 Å and O ··· O and C ··· O distances <3·6 Å

Distances between atoms in molecules:

A(1) at (x_1, y_1, z_1)		and *A*(2) at (x_2, y_2, z_2)			
H(25) ··· Br(26)	3·19	C(5) ··· H(21)	3·03		
		C(6) ··· H(21)	3·03		
		H(24) ··· C(11)	3·20		
		H(24) ··· C(12)	3·14		
		H(24) ··· C(13)	3·23		
		H(23) ··· C(14)	3·13		
A(1)		and *B*(1) at ($-x_1$, $1 - y_1$, $1 - z_1$)			
C(13) ··· H(19)	3·22				
C(14) ··· H(19)	2·96				
C(16) ··· H(22)	3·12				
A(2)		and *C*(2) at ($1 - x_2$, $2 - y_2$, $1 - z_2$)			
H(19) ··· Br(26)	3·34	C(14) ··· H(19)	3·01		
		C(16) ··· H(22)	3·18		
A(1)		and *D*(1) at (x_1, $-1 + y_1$, z_1)			
C(6) ··· C(3)	3·63	C(5) ··· H(22)	3·11	H(20) ··· O(10)	2·82
C(15) ··· C(12)	3·64	C(6) ·· H(19)	3·05	H(23) ··· O(10)	2·77
		C(6) ··· H(22)	3·12	H(28) ··· O(10)	2·85
		C(15) ··· H(24)	3·04	H(20) ··· H(22)	2·79
		C(16) ··· H(24)	3·15	H(21) ··· H(19)	2·74
		H(21) ··· C(3)	3·07	H(27) ··· H(24)	2·78
		H(27) ··· C(12)	3·10		
		H(27) ··· C(13)	3·24		
A(1)		and *D*(2) at (x_2, $-1 + y_2$, z_2)			
Br(26) ··· H(25)	3·34	C(11) ··· H(24)	3·20		
		C(12) ··· H(24)	3·22		
		C(14) ··· H(25)	3·04		
		C(15) ··· H(24)	3·04		
		H(21) ··· C(4)	3·14		
		H(21) ··· C(5)	2·90		
		H(21) ··· C(6)	3·12		
A(2)		and *D*(2)			
C(6) ··· C(3)	3·64	C(5) ··· H(22)	3·21	H(20) ··· O(10)	2·84
C(15) ··· C(12)	3·65	C(6) ··· H(19)	3·07	H(23) ··· O(10)	2·70
		C(6) ··· H(22)	3·21	H(28) ··· O(10)	2·88
		C(15) ··· H(24)	3·05	H(20) ··· H(22)	2·81
		C(16) ··· H(24)	3·11	H(21) ··· H(19)	2·72
		H(21) ··· C(3)	3·04	H(27) ··· H(24)	2·79
		H(27) ··· C(12)	3·12		
		H(27) ··· C(13)	3·18		
A(2)		and *E*(1) at ($-x_1$, $\frac{1}{2} + y_1$, $\frac{1}{2} - z_1$)			
Br(26) ··· Br(26)	3·81				
A(2)		and *F*(1) at (x_1, $\frac{1}{2} - y_1$, $-\frac{1}{2} + z_1$)			
Br(26) ··· C(1)	3·75	Br(26) ··· H(17)	2·93		
A(1)		and *G*(1) at ($-x_1$, $-y_1$, $1 - z_1$)			
C(3) ··· H(27)	3·06				
C(4) ··· H(27)	3·08				
F(2) at (x_2, $\frac{1}{2} - y_2$, $-\frac{1}{2} + z_2$)		and *H*(1) at ($1 - x_1$, $-y_1$, $1 - z_1$)			
H(18) ··· C(1)	3·19				
H(18) ··· C(2)	3·14				
F(2)		and *H*(2) at ($1 - x_2$, $-y_2$, $1 - z_2$)			
H(18) ··· H(17)	2·70				
C(2) ··· H(17)	3·02				
F(2)		and *I*(2) at ($1 - x_2$, $\frac{3}{2} + y_2$, $\frac{1}{2} - z_2$)			
C(3) ··· H(27)	3·11				
C(4) ··· H(27)	3·02				

The best plane equations of the phenyl (A), bromophenyl (B) and 1,3-enone groups and the deviations of the relevant atoms from these planes are in Table 2. Bond lengths and angles with their σ values are in Tables 3 and 4. Figures 1 and 2 show the packing arrangement down the [100] and [010] axes. Table 5 lists short molecular contact distances.

DISCUSSION

Bond Lengths and Angles.—The root-mean-square value of the estimated standard deviations in bond lengths (0·014 Å) compares well with the value obtained from the ' bond scatter ' defined as the root-mean-square deviation from the mean of the aromatic C–C bonds. The mean value of these 24 bonds is 1·394 Å with a root-mean-square deviation from the mean of 0·015 Å. A χ^2 test indicates no significant differences in the bond lengths of the two individual molecules; in fact, the ' bond scatter ' computed for the 17 pairs of equivalent bonds in the two molecules is somewhat smaller (0·010 Å) than the values already mentioned.

The means of bonds of the 1,3-enone systems compare well with those observed for similar molecules:[9] C(4)–C(7) 1·46, 1·455; C(7)–C(8) 1·33, 1·320; C(8)–C(9) 1·48, 1·477; C(9)–O(10) 1·24, 1·227; and C(9)–C(11) 1·50, 1·499 Å. The mean C–Br bond length (1·895 Å) agrees with values quoted in the literature, *e.g.*, bis-(*m*-bromobenzoyl)methane (1·901 Å),[10] *N*-(*p*-bromophenyl)sydnone (1·89 Å),[11] and 4-bromo-2′-nitrochalcone (1·94 Å).[12]

The aromatic C–C–C angles of ring A in the two molecules show no significant deviation from the expected value of 120°. In ring B however, the deviation at C(14) is large and is due probably to the bromine substituent. This effect has been observed in other bromobenzene compound, see *e.g.*, refs. 10 and 12 (122·7, 123°), and also in some chlorobenzenes.[13,14] A similar effect involving another electron-withdrawing group ($-\mathrm{NO}_2$) has been observed and discussed.[15] The bond angles in the 1,3-enone system are similar to those found in related molecules.[9]

The match in bond lengths and angles in the two molecules of this structure and the agreement with those observed in other structure are reflected in the 1,3- and 1,4-interactions which show a high degree of constancy in a series of molecules.[9]

Molecular Shape.—The molecules adopt the cisoid conformation, in agreement with the majority of other reported chalcone structures. The shape of the two molecules in the asymmetric unit is the same, the slight differences in bond twist and planarity of the various molecular parts being insignificant. The molecule as a whole is not planar; the maximum deviation (0·6 Å) is centred at C(6). The phenyl rings are planar within their estimated standard deviations while C(7), C(9), and the Br atoms deviate significantly from their respective phenyl groups; there are also appreciable deviations from planarity in the 1,3-enone system (Table 2).

The essential difference in shape between the present molecule (I) and other chalcones such as the parent compound[16] and its *p*-methoxy-derivative[8] lies in the large twist (26°) about C(9)–C(11) and the large angle (50°) between the phenyl rings in (I) as compared to typical values of 4 and 11° in the unsubstituted chalcone.

Packing Arrangement.—The two molecules in the asymmetric unit [designated by *A*(1) and *A*(2) in Table 5 and in Figures 1 and 2] are related by a pseudo-*b*-glide nearly normal to the *a* axis. The structure may be conveniently described in terms of molecular stacks along [010] consisting of *A*(1) and *A*(2) molecules and their symmetry-related stacks. These stacks are locked together by the bromine atoms spiralling along the 2_1 axes at $(0y\,\frac{1}{4})$ and $(0y\,\frac{3}{4})$. Other short contacts between the stacks are mainly of the Br · · · H and C · · · H types.

[2/384 *Received*, 21*st February*, 1972]

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