

2-Bromobenzophenone

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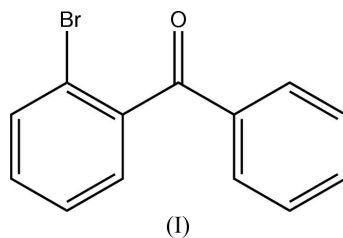
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.038
 wR factor = 0.064
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Details of the crystal structure and quantum chemistry calculations of the title molecule, $\text{C}_{13}\text{H}_9\text{BrO}$, illustrate the effects of intermolecular interactions and the substitution of one of the two aromatic rings on the molecular conformation. The asymmetry of the molecule is documented by the two $\text{C}_{\text{aryl}}-\text{C}_{\text{aryl}}-\text{C}=\text{O}$ torsion angles of -68.3 (5) and -17.6 (6) $^\circ$. A $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond [$\text{H}\cdots\text{O} = 2.5$ Å, $\text{C}\cdots\text{O} = 3.412$ (5) Å and $\text{C}-\text{H}\cdots\text{O} = 174^\circ$] and a $\text{C}-\text{H}\cdots\pi$ contact involving the H atom at position 4 of the substituted ring and the π -system of the unsubstituted ring of an adjacent molecule [$\text{H}\cdots\text{Cg} = 2.96$ Å, $\text{C}\cdots\text{Cg} = 3.806$ (5) Å and $\text{C}-\text{H}\cdots\text{Cg} = 153^\circ$; where Cg is the centroid of the unsubstituted ring] are observed in the crystal structure.

Comment

Benzophenones are good models for the study of conformational flexibility. They have been studied because of their potential applications, particularly in non-linear optics (Babu *et al.*, 2004; Kaminskii *et al.*, 2002). The helical propeller geometry of the isolated molecules is the result of a balance between the conjugation and steric interactions. The rotation of the aromatic rings is characterized by torsion angles defined relative to the carbonyl group plane. It is generally accepted that these angles are the key parameters that define the electronic configuration and the energetics of the molecule (Rappoport *et al.*, 1990; Weitzel & Bässler, 1986).



It was interesting to study the crystal structure of the title compound, (I), because substitution at the 2-position can promote steric hindrance that results in a large asymmetry of the molecule (viewed along the $\text{C}=\text{O}$ bond). The title molecule is indeed asymmetric (Fig. 1), as a result of the conjugation of the unsubstituted aromatic ring with the $\text{C}=\text{O}$ bond. Bond lengths $\text{C1}-\text{C1b}$ [1.480 (5) Å] and $\text{C1}-\text{C1a}$ [1.519 (4) Å] are different; these values are comparable with those in the literature [*cf.* 1.476 Å quoted by Bürgi & Dunitz (1994) for a conjugated $\text{C}_{\text{sp}2}-\text{C}_{\text{aryl}}$ bond, and 1.491 Å for a non-conjugated bond]. The torsion angle involving atoms of

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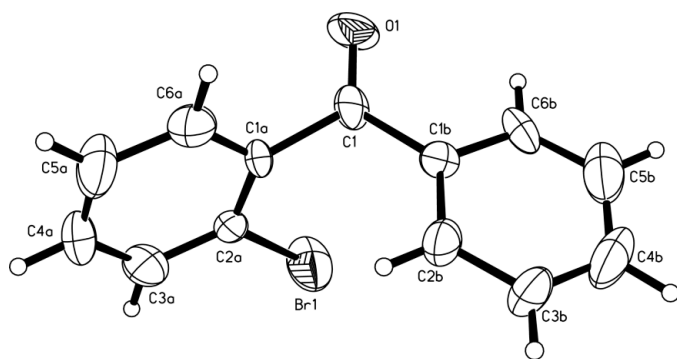


Figure 1
A view of the title molecule, showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme.

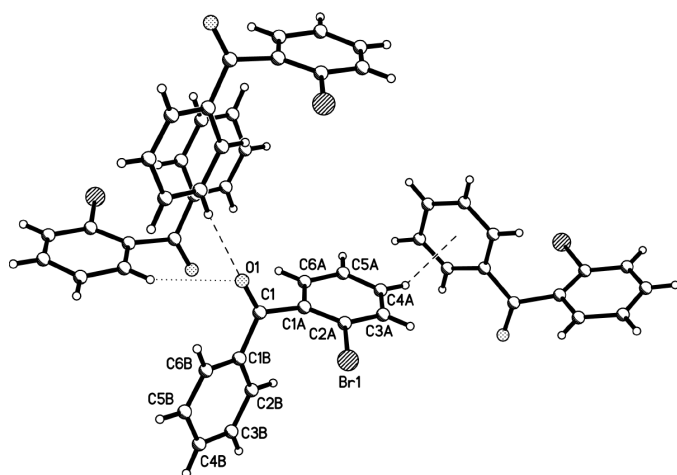


Figure 2
Weak hydrogen bonding (dashed lines) in the structure of (I).

the substituted aromatic ring, $O1-C1-C1a-C6a$, is unusually large [$-68.3(5)^\circ$], especially compared with the torsion angle of the unsubstituted aromatic ring [$O1-C1-C1b-C6b = -17.6(6)^\circ$]. These torsion angles are different from that of 4-bromobenzophenone (Ebbinghaus *et al.*, 1997), where the molecule is slightly asymmetric (the above-mentioned angles are -21.6 and -28.1°).

The intermolecular contact (Table 2) $O1 \cdots H3B$ (2.45 \AA) satisfies the criteria given by Desiraju & Steiner (1999) for a $C-H \cdots O$ hydrogen bond, and the interaction $C4a-H4A \cdots \pi$ (the normal distance = 2.96 \AA) corresponds with the known criteria (Babu, 2003; Castellano, 2004; Desiraju, 2002; Malone *et al.*, 1997) (Fig. 2). There is one unfavourable $O1 \cdots H6A$ contact of 2.71 \AA (Table 2 and Fig. 2).

It is interesting to compare the structures of (I) and the monochloro-substituted analogue (Pinkus *et al.*, 2004). Our comparison, based on calculations using *PLATON* (Spek, 2003), reveals that: (i) both compounds are isostructural; (ii) both molecules are asymmetric (the torsion angles, defined as above, for the chloro analogue are -61.35° for the substituted

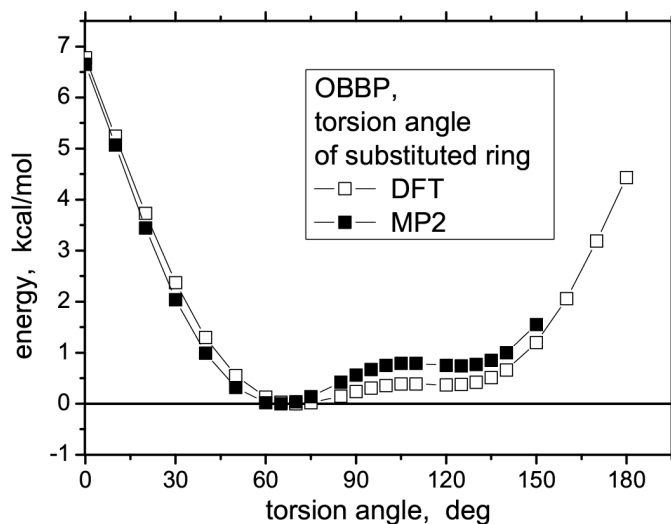


Figure 3
The global energy of *ortho*-bromobenzophenone (in the gas phase) as a function of the torsion angle $C2a-C1a-C1-C1b$ of the substituted aromatic ring. DFT data are obtained with the density functional theory method B3LYP/cc-pVDZ, MP2 data are obtained by single-point energy calculations on the MP2/cc-pVDZ level of the theory.

ring and -20.01° for the unsubstituted ring); (iii) all short contacts discussed above for (I) are comparable to the values for the crystal structure of *ortho*-chlorobenzophenone.

Theoretical calculations on (I) revealed two conformers of minimum energy: in one, the bromine is in steric contact with the hydrogen from the unsubstituted ring, whereas in the other, the bromine is not in contact, pointing upwards at the other side of the ring. Both conformers have enantiomers. In order to clarify to what extent the two possible conformers are close in energy and to recognize the conformational changes introduced in the solid state by crystal packing, we performed quantum chemical modelling of the isolated title molecule. The relaxed potential energy surface along the path of the $C2a-C1a-C1-C1b$ torsion angle was scanned using the program package *NWChem* (Straatsma *et al.*, 2003). The values of the above-mentioned torsion angles in the two minima were found to be 70.5 [*cf.* the angle of $70.0(5)^\circ$ in Table 1] and -122.1° . Comparison of a few calculated torsion angles with the analogous measured values in Table 1 reveals that the crystal packing has a substantial influence on the conformational parameters of the title molecule in the solid. This observation is in agreement with a low barrier between the two stable conformations. The favourable conformer was found (Fig. 3) to be more stable by $0.4 \text{ kcal mol}^{-1}$. This relatively low value results in a rather high concentration of the unfavourable conformation in the vapour or dilute solution: at room temperature it amounts to 34%. The estimated energy barrier between the two conformations is necessarily low. The frequency of flips between conformations in the gas phase at room temperature (which is close to the melting point of the title compound) should be very high. This might explain the quite uncommon reluctance of crystals to grow by sublimation *in vacuo*.

Experimental

As the source material, commercial *ortho*-bromobenzophenone (Shostka factory of Chemical Reactants, Ukraine) of nominal technical purity grade was used. As the first step, the material was purified by gradient sublimation in a reduced pressure of about 0.133 Pa. The compound showed a very unusual reluctance to crystallize. The melting point of 315 K corresponds to that quoted by Weast (1966).

Crystal data

C ₁₃ H ₉ BrO	$D_x = 1.559 \text{ Mg m}^{-3}$
$M_r = 261.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 24 reflections
$a = 7.836 \text{ (2) \AA}$	$\theta = 13\text{--}15^\circ$
$b = 16.833 \text{ (4) \AA}$	$\mu = 3.66 \text{ mm}^{-1}$
$c = 8.490 \text{ (2) \AA}$	$T = 293 \text{ (2) K}$
$\beta = 96.72 \text{ (2)^\circ}$	Plate, colourless
$V = 1112.3 \text{ (5) \AA}^3$	$0.35 \times 0.24 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Siemens P3/PC diffractometer	$R_{\text{int}} = 0.075$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: by integration (<i>XPREP</i> ; Siemens, 1991)	$h = 0 \rightarrow 9$
$T_{\text{min}} = 0.425, T_{\text{max}} = 0.585$	$k = 0 \rightarrow 20$
2111 measured reflections	$l = -10 \rightarrow 10$
1963 independent reflections	2 standard reflections every 98 reflections
1170 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2)]$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
1963 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
136 parameters	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Br1—C2a	1.893 (4)	C1a—C2a	1.367 (5)
O1—C1	1.197 (4)	C1a—C6a	1.379 (5)
C1—C1b	1.480 (5)	C1b—C6b	1.383 (5)
C1—C1a	1.519 (4)	C1b—C2b	1.398 (5)
O1—C1—C1b	121.6 (3)	C6a—C1a—C1	117.6 (3)
O1—C1—C1a	120.5 (3)	C6b—C1b—C2b	118.4 (4)
C1a—C1—C1b	117.7 (3)	C6b—C1b—C1	120.4 (4)
C2a—C1a—C6a	116.8 (3)	C2b—C1b—C1	121.2 (4)
C2a—C1a—C1	125.4 (3)	C1—C1a—C2a—Br1	4.3 (5)
O1—C1—C1a—C2a	106.4 (5)	C2a—C1a—C6a—C5a	−0.3 (6)
C1b—C1—C1a—C2a	−70.0 (5)	C1—C1a—C6a—C5a	174.8 (4)
O1—C1—C1a—C6a	−68.3 (5)	O1—C1—C1b—C6b	−17.6 (6)
C1b—C1—C1a—C6a	115.3 (4)	C1a—C1—C1b—C6b	158.8 (3)
C6a—C1a—C2a—C3a	−1.0 (6)	O1—C1—C1b—C2b	161.3 (4)
C1—C1a—C2a—C3a	−175.7 (4)	C1a—C1—C1b—C2b	−22.4 (5)
C6a—C1a—C2a—Br1	179.0 (3)		

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C3b—H3B \cdots O1 ⁱ	0.93	2.50	3.412 (5)	168
C6a—H6A \cdots O1 ⁱⁱⁱ	0.93	2.71	3.562 (5)	113
C4a—H4A \cdots Cg2 ⁱⁱⁱ	0.93	2.96	3.806 (5)	153

Symmetry codes: (i) $1+x, y, z$; (ii) $-x, 2-y, 2-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$. Cg2 is the centroid of the unsubstituted ring.

All H atoms were observed in a difference map and treated as riding, with C—H = 0.93 Å. $U_{\text{iso}}(\text{H})$ values were set equal to $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* and *XPREP* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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