

4,4'-Dibromobenzophenone at 293
and 103 K

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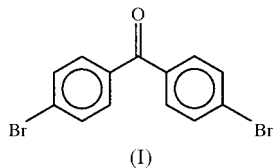
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The structure of 4,4'-dibromobenzophenone, $C_{13}H_8Br_2O$, was determined at two different temperatures (293 and 103 K). A phase transition was not detected in this temperature range. Its crystal structure was found to be isostructural with that of the diiodo analogue, but not with the structure of the dichloro derivative.

Comment

Molecules of 4,4'-halogenated-benzophenones and their precursor benzophenone, in accord with the hybridization of the atoms involved, should be planar. However, the steric hindrances introduced by the H atoms (overcrowding effect) have caused puckering of these molecules. The halogenated molecules exhibit C_2 symmetry with a crystallographic twofold axes through a carbonyl bond, whereas benzophenone reveals an approximate C_2 molecular symmetry. The puckering of the benzophenone skeleton can be illustrated by the dihedral angle between the two phenyl rings. In these compounds their values range from 48.9 to 55.8° (4,4'-difluorobenzophenone, 48.9°, Maginn & Davey, 1994; 4,4'-dichlorobenzophenone, room temperature phase, 50.5°, Granger & Coillot, 1985; 4,4'-dichlorobenzophenone, low temperature phase, 49.3°, Zúñiga & Criado, 1995; 4,4'-diiodobenzophenone, 50.1°, van der Velden & Noordik, 1979; benzophenone, 55.8°, Fleischer *et al.*, 1968). The existence of the phase transition of 4,4'-dichlorobenzophenone (Zúñiga & Criado, 1995) and the temperature-dependent Raman spectra of 4,4'-dibromobenzophenone (Volovšek *et al.*, 1995) motivated us to investigate the X-ray structure of 4,4'-dibromobenzophenone, (I), in the temperature range 100–293 K. In order to provide more information,



the unit cell and the possible phase transition were examined at 293, 223, 163 and 103 K. For the unit-cell determinations 25 reflections at a high θ angle were used and an additional ten reflections were examined on possible intensity changes. The

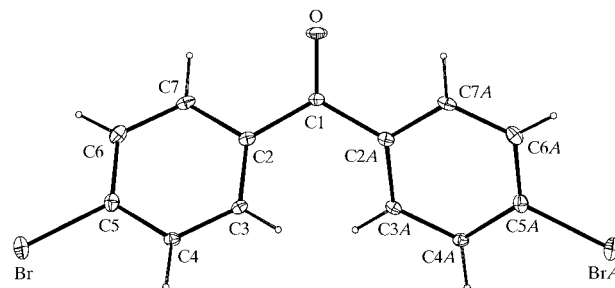


Figure 1

The structure of the title compound (I) determined at 103 K. Displacement ellipsoids are scaled at the 30% probability level.

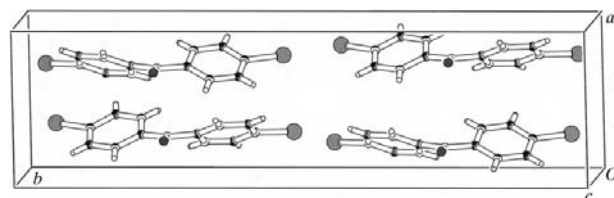


Figure 2

Crystal packing shows polar regions composed of Br atoms separated by aromatic systems.

correlation of the unit-cell dimensions with temperature revealed that $\Delta a/a \approx 5\Delta b/b \approx 5\Delta c/c$. An assumption that this effect might be related to the changes of the dihedral angle between phenyl rings was not justified by the crystal structure determination at two different temperatures [50.10 (12) and 49.60 (15)° at 293 and 103 K, respectively]. Thus, our data have not revealed a change of the space group ($Ccc2$).

The *ORTEP* (Johnson, 1976) plot (Fig. 1) and crystal packing (Fig. 2) of 4,4'-dibromobenzophenone show the structure solved from low-temperature data. The crystal packing (Fig. 2) is determined by van der Waals interactions. This type of packing is isostructural with that of the diiodo analogue (van der Velden & Noordik, 1979) but not with the packing of the difluoro (Maginn & Davey, 1994) and dichloro (Granger & Coillot, 1985; Zúñiga & Criado, 1995) analogues. The carbonyl bonds of the dibromo and diiodo analogues are oriented along the polar twofold axes running along the c axes (in the space group $Ccc2$, Fig. 2). As a consequence of the space group symmetry, a uniform orientation of the parallel polar groups (carbonyl) is maintained.

Experimental

The title compound, commercially available (ICN Pharmaceuticals Inc., Plainview, NY) was recrystallized from pure benzene solution at room temperature. Using the same sample the structure determination was performed at 293 and 103 K.

Compound (I) at 293 K

Crystal data

$C_{13}H_8Br_2O$
 $M_r = 339.99$
 Orthorhombic, $Ccc2$
 $a = 7.3969$ (4) Å
 $b = 26.7030$ (9) Å
 $c = 6.0594$ (3) Å
 $V = 1196.85$ (10) Å³
 $Z = 4$
 $D_x = 1.887$ Mg m⁻³

Cu $K\alpha$ radiation
 Cell parameters from 25
 reflections
 $\theta = 43.90$ – 47.71°
 $\mu = 8.38$ mm⁻¹
 $T = 293$ K
 Prism, colourless
 $0.180 \times 0.138 \times 0.072$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical (PLATON; Spek, 1998)
 $T_{\min} = 0.386$, $T_{\max} = 0.591$
 744 measured reflections
 679 independent reflections

Refinement

Refinement on F^2
 $R(F) = 0.022$
 $wR(F^2) = 0.066$
 $S = 1.052$
 679 reflections
 91 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.3857P]$
 where $P = (F_o^2 + 2F_c^2)/3$

581 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 74.08^\circ$
 $h = 0 \rightarrow 9$
 $k = -33 \rightarrow 0$
 $l = 0 \rightarrow 7$
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.8%

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.00085 (11)
 Absolute structure: Flack (1983)
 Flack parameter = $-0.02(4)$

Refinement

Refinement on F^2
 $R(F) = 0.019$
 $wR(F^2) = 0.053$
 $S = 1.157$
 649 reflections
 91 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.5575P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.00057 (8)
 Absolute structure: Flack (1983)
 Flack parameter = 0.00 (4)

The C–H distances are in the range 0.90 (3)–0.97 (4) Å.

For both data sets, data collection: CAD-4 EXPRESS (Enraf–Nonius, 1992); cell refinement: CELDIM in CAD-4 EXPRESS; data reduction: HELENA (Spek, 1997); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1996); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1998); software used to prepare material for publication: PLATON.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1339). Services for accessing these data are described at the back of the journal.

Compound (I) at 103 K

Crystal data

$\text{C}_{13}\text{H}_8\text{Br}_2\text{O}$
 $M_r = 339.99$
 Orthorhombic, *Ccc2*
 $a = 7.2242(2) \text{ \AA}$
 $b = 26.5957(9) \text{ \AA}$
 $c = 6.0118(2) \text{ \AA}$
 $V = 1155.06(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.955 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 44.07\text{--}47.82^\circ$
 $\mu = 8.68 \text{ mm}^{-1}$
 $T = 103(3) \text{ K}$
 Prism, colourless
 $0.180 \times 0.138 \times 0.072 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical (PLATON; Spek, 1998)
 $T_{\min} = 0.349$, $T_{\max} = 0.581$
 713 measured reflections
 649 independent reflections

630 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 73.92^\circ$
 $h = 0 \rightarrow 9$
 $k = -32 \rightarrow 0$
 $l = 0 \rightarrow 7$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.2%

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