Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Polymorphism of 4-bromobenzophenone

Mikhail A. Strzhemechny,[a]* Vyacheslav N. Baumer,[a,b] Anatoli A. Avdeenko,[a] Oleg S. Pyshkin,[a] Roman V. Romashkin[a] and Lyubov M. Buravtseva[a]

[a]Verkin Institute for Low Temperature Physics and Engineering, 47 Lenin Avenue, Kharkov 61103, Ukraine, and [b]Institute for Single Crystals, 60 Lenin Avenue, Kharkov 61001, Ukraine

Correspondence e-mail: strzhemechny@ilt.kharkov.ua

Received 21 April 2006
Accepted 14 December 2006

A combination of single-crystal and powder X-ray diffractometry was used to study the structure of two polymorphs of 4-bromobenzophenone over the temperature range from 100 to 300 K. One of the polymorphs of the title compound was known previously and its structure has been determined at room temperature [Ebbinghaus *et al.* (1997). *Z. Kristallogr.* **212**, 339–340]. Two crystal growth methods were employed, one of which (a modification of the Bridgman–Stockbarger technique) resulted in single crystals of a previously unknown structure. The basic physical properties of the stable polymorph are: growth method, from 2-propanol solutions or gradient sublimation; space group, monoclinic $P2_1/c$; melting point, T_m = 355.2 K; X-ray density (at 100 K), D_x = 1.646 g cm^{-3}. The same properties of the metastable polymorph (triclinic $P\overline{1}$) are: growth method, modified Bridgman–Stockbarger method; X-ray density (at 100 K), D_x = 1.645 g cm^{-3}; T_m = 354 K. Thermograms suggest that the melting of the metastable form is accompanied by at least a partial crystallization presumably into the monoclinic form; the transformation is therefore monotropic. Analysis of short distances in both polymorphs shows that numerous weak hydrogen bonds of the C—H$\cdots\pi$ type ensure additional stabilization within the respective planes normal to the longest dimension of the molecules. The strong temperature dependence of the lattice constants and of the weak bond distances in the monoclinic form suggest that the weak bond interactions might be responsible for both the large thermal expansion within plane *bc* and the considerable thermal expansion anisotropy.

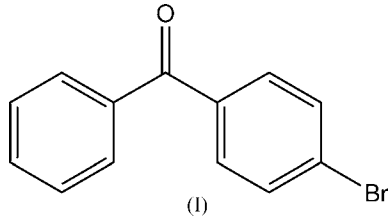
1. Introduction

The polymorphism of organic crystals, which is quite a common phenomenon, is at present an issue under intensive study. Substituted derivatives of benzophenone are no exception in this sense. However, given the rather large number of substituted benzophenone crystals for which the structure is known (Allen, 2002), examples of polymorphs in these organic solids are scarce. Considering the importance of substituted benzophenones for many scientific and industrial applications (Turro, 1992; Zhan *et al.*, 2000), further investigations in this direction are desirable. In general, this is especially true for studies which could help understand the solidification mechanisms and work out reliable growth procedures and methods capable of producing new stable or, at least metastable, polymorphs of various organic crystals.

To date, there are a few examples of polymorphs of benzophenone derivatives. For instance, unsubstituted benzophenone (BP), in which polymorphism in organic crystals was first observed, has stable orthorhombic ($P2_12_12_1$; α)

and metastable monoclinic ($C2/c$; β) polymorphs (Lobanova, 1968; Kutzke *et al.*, 2000) with a monotropic transition $\beta \Rightarrow \alpha$. A similar relation exists between polymorphs of 4-methylbenzophenone (4-MBP), also with a monotropic $\beta \Rightarrow \alpha$ transformation; the stable α phase is $P2_1/c$ monoclinic (Ito *et al.*, 1987) and the metastable β phase is $P3_1$ or $P3_2$ trigonal (Kutzke *et al.*, 1996). There is an example of two polymorphs with a reversible displacive ($C2/c \Leftrightarrow I2/c$) phase transition between them in 4,4′-dichlorobenzophenone (Zúñiga & Criado, 1995; Mitkevich *et al.*, 1999). Polymorphism in 2-amino-5-nitrobenzophenone crystals has its own history. The structure, first determined by Dvorkin *et al.* (1985), was found to be monoclinic, space group (after relabeling) $P2_1/b$ (polymorph *A*). Cox *et al.* (1998) found a new polymorph (*B*), which has the same symmetry but substantially different lattice parameters. Later, Cox & Wardell (2000) redetermined the structure of polymorph *A* to show that their lattice parameters of this crystal (let us call it *A*′) differ appreciably from those of Dvorkin *et al.* (1985). Since Dvorkin *et al.* (1985) did not describe their sample growth procedure, the reasons for those discrepancies remain unknown. It is interesting (Kutzke *et al.*, 2000) that the metastable monoclinic $C2/c$ in BP and the stable $P2_1/c$ in 4-MBP are racemic (*i.e.* containing both enantiomers in equal parts), whereas their counterparts (stable orthorhombic $P2_12_12_1$ in BP and metastable trigonal $P3_1$ in 4-MBP) are enantiomorphic (*i.e.* consisting of only one enantiomer type).

Previously, the structure of 4-bromobenzophenone [4BrBP; see (I)] has been determined at room temperature by Ebbinghaus *et al.* (1997) on a single-crystal sample grown from a 2-propanol solution. The structure was found to be monoclinic with space group $P2_1/c$ and the following lattice parameters: a = 12.138 (1), b = 14.766 (2), c = 6.174 (1) Å, β = 97.63 (1)°, Z = 4, V = 1096.8 Å^3, D_x = 1.582 g cm^{-3} (our estimate). It is well known (Bernstein, 2002; Banga *et al.*, 2004; Mullin, 2001) that growth conditions can crucially influence the emerging structure. Therefore, when growing 4BrBP crystals we tried to vary growth procedures and parameters in order to look for possible new (*meta*) stable polymorphs of the title compound. The two methods employed (see §2) did not involve any solutions and one of them yielded a new polymorph. In view of certain X-ray data collection instabilities (varying reflection intensities) observed at room temperature and slightly below, we performed successful single-crystal structure measurements on the new polymorph only at a temperature of 100 K. Most likely, those instabilities were caused by a partial solution of the sample in the fixing glue. No instabilities were observed at 100 K or even at 250 K.



(I)

Determination of the temperature-related changes in the lattice parameters helps to gain insight into the mechanisms and interactions that control the lattice dynamics of the solid (Mitkevich *et al.*, 1999; Perić & Kojić-Prodić, 2000). We determined the structure of the monoclinic polymorph samples grown by gradient sublimation at several temperatures.

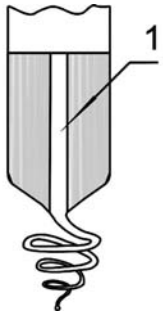


Figure 1
Schematic view of the lower part of the crystallization ampoule in the Bridgman–Stockbarger method. The transparent vertical slab 1 is the growing crystal. The surrounding gray matter is a fine-grained polycrystal.

2. Experimental

2.1. Crystal growth

Commercial *para*-bromobenzophenone (Factory of Chemical Reactants, Lviv, Ukraine) of the nominal technical purity grade was used as the source material. According to the CRC Handbook (Weast, 1986), the melting temperature of 4BrBP is 355.7 K. Thermography measurements (Gurevich, 2006) gave 355.2 ± 0.2 K The material was purified by multiple (50 passes) zone melting as well as by gradient sublimation (McGhie *et al.*, 1974) at a reduced pressure of ∼ 0.133 Pa. The latter procedure was essentially the same as employed for subsequent sample growth. Single crystals of pure 4BrBP were grown using both the gradient sublimation (McGhie *et al.*, 1974) and vertical Bridgman–Stockbarger (Scheel, 2003) techniques. Samples from every growth batch were rapidly examined by powder X-ray diffraction in order to optimize the relevant growth procedures. Under gradient sublimation, the material was kept slightly above or below the melting point; the temperature of the cold end was varied from 453 to 503 K; two sublimation tubes were used, 95 and 820 mm long. The crystals grown with gradient sublimation were transparent, needle-shaped with typical dimensions (0.2–0.3) × (0.3–0.5) × (2–4) mm. The tube length did not significantly affect the shape and dimension of the crystals, which were found to be monoclinic.

In the Bridgman–Stockbarger's method, the bottom part of the crystallization ampoule contained a spiral capillary. As the crystallization zone moved very slowly (30 mm during ∼ 100 h) upwards, a clear transparent plate-shaped crystal emerged, immersed in an opaque matter, as shown in Fig. 1. Its surroundings looked like a glass or a polycrystal made up of very small crystallites. After this single-crystal plate was cut

Table 1
Crystal data, physical properties and experimental details for the two polymorphs of 4-bromobenzophenone.

All data can be found in the CIF file.

	Stable form	Metastable form
Crystal data		
Chemical formula	$C_{13}H_9BrO$	$C_{13}H_9BrO$
Formula weight	261.10	261.10
Crystal dimensions (mm)	0.15 × 0.10 × 0.02	0.40 × 0.20 × 0.04
Crystal shape, color	Needles, colorless	Plate, colorless
Melting point (K)	355.2 ± 0.1† 355.7§	354.0 ± 0.2‡
Growth method	Gradient sublimation 2-propanol solution¶	Bridgman–Stockbarger
Temperature (K)	100 (2)	100 (2)
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
a, b, c (Å)	12.092 (2), 14.343 (3), 7.293 (2)	6.106 (1), 6.124 (1), 12.100 (2)
α, β, γ (°)	90.00, 97.26 (3), 90.00	98.20 (2), 98.74 (1), 91.11 (2)
Z	4	2
V (Å^3)	1053.7 (4)	526.6 (2)
D_x (g cm^{-3})	1.647	1.646
Radiation	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.869	3.868
Data collection		
Diffractometer	XCalibur3, CCD detector	XCalibur3, CCD detector
Collection method	ω scan	ω scan
Absorption correction	Empirical (using measured intensities)	Empirical (using measured intensities)
T_{min}	0.235	0.110
T_{max}	0.734	0.576
No. of measured, independent, and observed reflections	12 546, 3444, 2253	5351, 3710, 2748
Criterion for observed reflections	$I > 2.0\sigma$	$I > 2.0\sigma$
R_{int}	0.121	0.069
θ_{max} (°)	32.1	34.0
Refinement		
Refinement	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.085, 0.294, 1.00	0.078, 0.204, 1.00
No. of reflections	3444	3710
No. of parameters	136	136
H-atom treatment	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.090P)^2 + 3.010P]^{-1}$, where $P = F_o^2 + F_c^2$	$w = [\sigma^2(F_o^2) + (0.090P)^2 + 3.010P]^{-1}$, where $P = F_o^2 + F_c^2$
$(\Delta/\sigma)_{max}$	< 0.0001	< 0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.98, −0.91	1.47, −0.86
Extinction method	None	None

† Gurevich (2006). ‡ Gurevich (2006). This melting is presumably followed by crystallization into a new phase, which finally melts slightly above 355.0 K. § Weast (1986). ¶ Ebbinghaus *et al.* (1997).

out of its 'matrix', its dimensions [approximately 1 × 7 × (10–12) mm] were substantially larger than those grown by sublimation. This large single crystal proved to have a triclinic lattice. A reminder is needed here that the samples studied by Ebbinghaus *et al.* (1997) were grown from 2-propanol solutions, other sample preparation details being unknown. In Table 1 we summarize the structural and other physical properties of both 4BrBP polymorphs.

In §2.2 we discuss in detail the melting behavior of both forms. Here we only note that if triclinic crystals were melted and then allowed to recrystallize, the emerging solid was monoclinic. Intensive grinding of triclinic crystals also resulted in a powder with a considerable fraction of the monoclinic form. This allowed us to conclude that the *t*-form is unstable whereas the *m*-form is stable.

2.2. Diffraction experiments

The single-crystal diffraction measurements were performed on an XCalibur3 (Oxford Diffraction) machine; a Siemens D500 diffractometer was employed for X-ray powder diffraction experiments to check the structure and quality or the phase composition of the crystals after growth and various manipulations. The temperature stabilization in powder diffraction experiments was better than ±0.1 K; the temperature was varied from 100 to 300 K.

We succeeded in determining the structure of the new 4-bromobenzophenone polymorph at 100 K. Details of single-crystal diffraction experiments are summarized in Table 1.

In addition, we determined the lattice parameters as well as the conformational and packing parameters of the known stable monoclinic polymorph at two temperatures (100 and 250 K) and data of Ebbinghaus *et al.* (1997) for T = 293 K. These samples were grown by gradient sublimation. The room-temperature lattice parameters were found to be essentially the same as determined by Ebbinghaus *et al.* (1997) on a sample grown from 2-propanol solution. The following computer programs were used: *CrysAlis* (Oxford Diffraction, 2005), *SHELXS*90 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1999).

3. Results and discussion

Some of the molecular and crystal structure data are presented in Figs. 2–4 as well as in Tables 1–3.[1]

When comparing the structures of the triclinic (hereinafter, *t*-form, for short) and monoclinic (*m*-form) polymorphs at 100 K (see Figs. 3 and 4), at first glance the *t*-form seems to be a somewhat distorted replica of the *m*-form, as might be inferred after a proper axis nomenclature interchange ($a \leftrightarrow c$) and considering the twice fewer number of molecules in the unit cell of the *t*-form. However, a more careful inspection of both racemic structures shows that the two motifs differ. Both structures in Figs. 3 and 4 are convenient to inspect if viewed almost parallel to axis c in the *m*-form and to axis a in the *t*-form. Labeling the planes, which are drawn through molecules of the same orientation, by the general direction of the bromines (essentially up or down along the respective axes), one can see that in the *t*-form the Br-up and Br-down rows alternate, while in the *m*-form they alternate in pairs. This

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: RY5005). Services for accessing these data are described at the back of the journal.

essential difference is important when we consider the possible mutual transformations of the two polymorphs. It can be easily understood that any displacements of sheets, as in 4,4′-dichlorobenzophenone (Zúñiga & Criado, 1995; Mitkevich *et al.*, 1999), or change in chirality accompanied by local displacements, as in benzophenone (Kutzke *et al.*, 2000), cannot transform one form into the other. The only mechanism that could lead to the transformation must involve rotation of molecules around axes normal to the C1*a*—C—C1*b* plane, which is energetically impossible in a regular crystal. Therefore, a possible transformation to the stable form can occur only *via* an amorphous (in other words, liquid) phase. Preliminary thermographic measurements (Gurevich, 2006) show that the metastable form undergoes a destructive transition (melting) at T_m = 354.0± 0.2 K and, presumably, crystallizes into another form, which finally melts at a temperature which is very close to the melting point of the pure *m*-form, T_m = 355.2 ± 0.2 K. The last value differs from the handbook entry (Weast, 1986) of 355.7 K. More accurate studies of these transformations are needed. It should be noted here that a like situation was reported by Zhang *et al.*

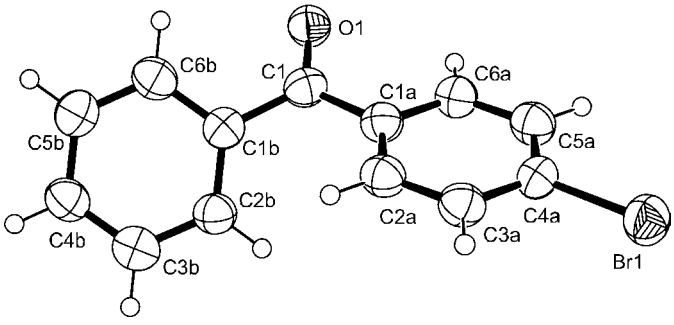


Figure 2
A view of the title molecule, showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme (triclinic polymorph, T = 100 K).

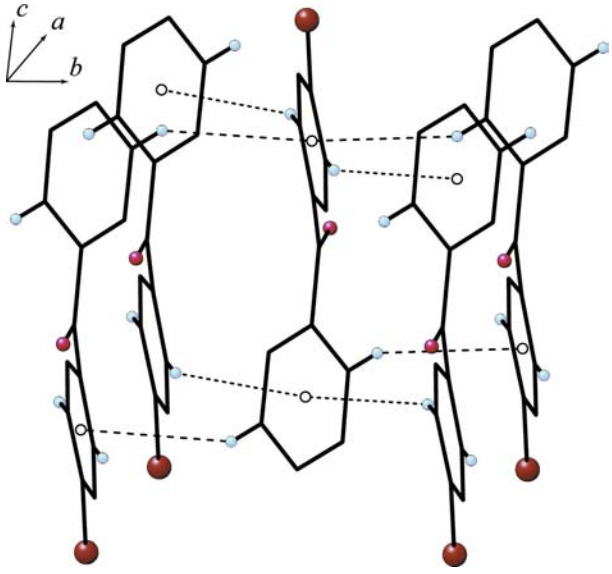


Figure 3
The structure of the *t*-form as viewed almost parallel to axis *a*. The large and small darker spheres are, respectively, Br and O atoms; the lighter spheres are the H atoms that participate in C—H···π weak hydrogen bonds. The planes with C4*b*—Br bonds pointing upward alternate with the planes in which those bonds are oriented downward.

Table 2
Some bond distances (Å) and bond angles (°) of the new triclinic 4BrBP polymorph in comparison with the respective values of the previously known monoclinic crystal.

Parameter	*t*-form, 100 K (this work)	*m*-form, 100 K (this work)	*m*-form, 293 K (Ebbinghaus *et al.*, 1997)
Br1—C4*a*	1.898 (4)	1.881 (5)	1.889 (5)
O1—C1	1.223 (6)	1.212 (6)	1.225 (6)
C1—C1*a*	1.500 (6)	1.496 (8)	1.498 (7)
C1—C1*b*	1.487 (6)	1.501 (8)	1.477 (8)
O1—C1—C1*b*	120.2 (4)	119.0 (5)	119.9 (5)
O1—C1—C1*a*	119.0 (4)	120.2 (5)	118.0 (5)
C2*a*—C1*a*—C6*a*	118.9 (4)	119.4 (5)	118.8 (5)
C1*a*—C1*a*—C6*b*	118.99 (4)	119.4 (5)	118.8 (5)
C2*b*—C1*b*—C6*b*	118.2 (4)	119.6 (5)	118.8 (5)
O1—C1—C1*a*—C2*a*	156.1 (5)	155.0 (6)	153.5 (6)
O1—C1—C1*b*—C2*b*	147.5 (5)	148.7 (6)	148.5 (6)
C1*a*—C1—C1*b*—C2*b*	32.7 (7)	33.0 (8)	32.8 (8)
C1*b*—C1—C1*a*—C2*a*	23.7 (7)	29.2 (7)	25.3 (8)
C6*a*—C1*a*—C2*a*—C3*a*	0.1 (7)	0.2 (8)	1.4 (7)
C6*b*—C1*b*—C2*b*—C3*b*	1.0 (7)	2.4 (8)	2.3 (8)

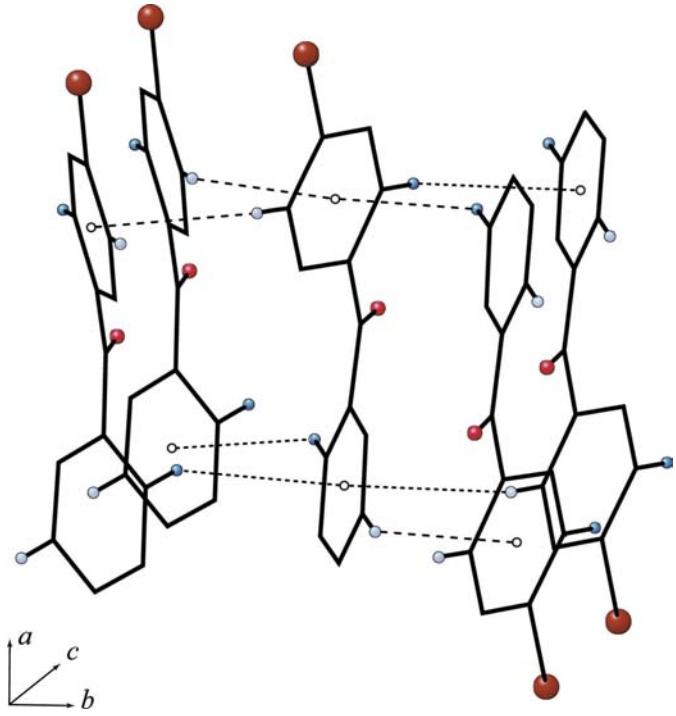


Figure 4
The structure of the *m*-form as viewed almost parallel to axis *c*. The symbols are the same as in Fig. 3. Unlike in the *t*-form, the planes with C4*b*—Br bonds pointing upward go in adjacent pairs, as do the planes with bromines pointing downward.

(1999) for mutual transformations of the polymorphs of the 4,4′-dihydroxybenzophenone/4,13-diaza-18-crown-6 complex.

The volumes per molecule for the two polymorphs are very close at any temperature: at 100 K V_m = 263.3 (1) Å^3 for the *t*-form and V_m = 263.4 (1) Å^3 for the *m*-form. The general rule that the stable form must have a denser packing does not apply to 4BrBP; a similar situation is with the polymorphism in 4-methylbenzophenone (Kutzke *et al.*, 1996). The considerations of racemic *versus* enantiomorphic packing (Brock *et al.*, 1991) do not apply to 4BrBP, both polymorphic forms being racemic.

In Table 2 we compare some of the molecular structure parameters of the two polymorphs at 100 K. The difference between the torsion angles (O1—C1—C1*a*—C2*a* and O1—C1—C1*b*—C2*b*) in the *m*-form increases with cooling, yet staying smaller than in the *t*-form at any temperature. Since other geometric parameters do not differ essentially, we think that the larger twist-angle difference in the *t*-form is a result of more stringent packing restrictions. It should be noted here that the torsion angle differences (from 5 to 8°) in the 4-bromobenzophenone molecule, either in the free state or in the crystal, are by far smaller than in the 2-bromobenzophenone molecule (Baumer *et al.*, 2005), amounting to 50.7° at room temperature.

There are a few short contacts in the *t*-form structure (see Table 3 and Fig. 3) affecting the packing. *PLATON* (Spek, 2003) shows a shortened C—H···Br contact but, according to the existing notions (Nangia, 2002), this contact can hardly promote a weak bonding. Another two contacts of the type C═O···H—C by all the existing criteria (Desiraju & Steiner, 1999; Babu, 2003) are capable of forming a weak hydrogen bond, especially the first one quoted in Table 3. If the second one in the same column is also treated as a weak bond, then we have a competitive bifurcated weak bond, which is typical of some substituted benzophenones (for instance, Baumer *et al.*, 2005). There is a wealth of C—H···π contacts in the *t*-form structure: every phenyl ring on both of its sides receives weak bonds from the C—H groups at positions 3 and 6 of the respective neighbor molecules. At the same time, every C—H group at positions 3 and 6 on both phenyl rings of the reference molecule contributes to the weak bonds towards the π systems of the respective neighbor molecules. Summing up, molecules in the triclinic polymorph form bound sheets extending almost parallel to plane *ab*: all weak bonds operate exclusively within these sheets.

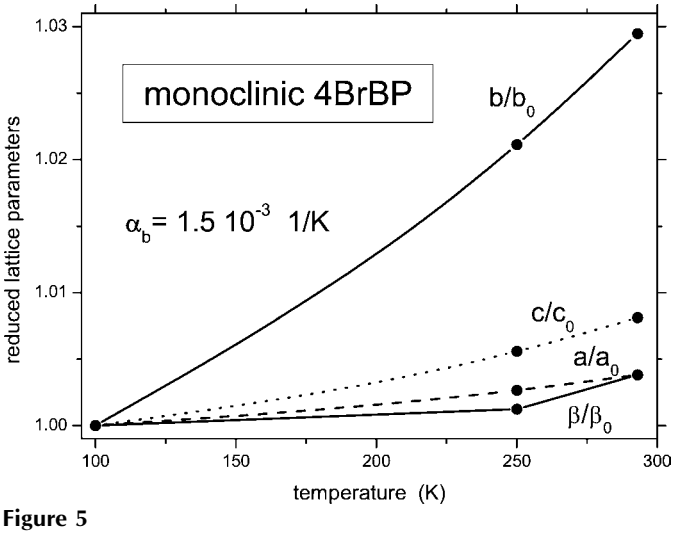


Figure 5
Variation of the relative lattice parameters of monoclinic 4BrBP with temperature. The respective reduction values are those at $T = 100K$. The error bars (of order 10^{-4}) are a little wider than the curve thickness.

Table 3
Hydrogen-bonding contact distances (Å) and angles (°), involving the respective centroids C_g in the triclinic and monoclinic polymorphic crystals of 4BrBP at 100 K.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H—*A*
Triclinic				
C3*a*—H3*a*···C_g2^{i}	0.95	2.89	3.630 (5)	136
C3*b*—H3*b*···C_g1^{ii}	0.95	2.91	3.614 (5)	132
C6*a*—H6*a*···C_g2^{iii}	0.95	2.89	3.579 (5)	131
C6*b*—H6*b*···C_g1^{iv}	0.95	2.78	3.460 (5)	129
C2*a*—H2*a*···O1^{v}	0.95	2.63	3.183 (6)	118
C2*b*—H2*b*···O1^{v}	0.95	2.72	3.380 (6)	127
Monoclinic				
C3*a*—H3*a*···C_g2^{vi}	0.95	2.78	3.502 (6)	134
C3*b*—H3*b*···C_g1^{vii}	0.95	2.86	3.569 (6)	133
C6*a*—H6*a*···C_g2^{viii}	0.95	2.80	3.512 (5)	132
C6*b*—H6*b*···C_g1^{ix}	0.95	2.84	3.460 (5)	131
C2*a*—H2*a*···O1^{x}	0.95	2.67	3.189 (7)	115
C2*b*—H2*b*···O1^{x}	0.95	2.75	3.407 (7)	129

Symmetry codes: (i) $1-x, 2-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $2-x, 1-y, -z$; (iv) $2-x, 2-y, -z$; (v) $-1+x, y, z$; (vi) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (vii) $-x, 1-y, 2-z$; (viii) $-x, 1-y, 1-z$; (ix) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (x) $x, y, -1+z$.

Short contacts in the *m*-form were not analyzed in the original paper by Ebbinghaus *et al.* (1997). As can be seen from Table 3 and Fig. 4, the set of weak contacts in the *m*-form principally coincides with that of the *t*-form, stabilizing the structure into weakly bound sheets stretching within plane *bc*.

The attractive interaction of antiparallel carbonyl dipoles also contribute to the stabilization of the structure. Making use of our previous calculations (Avdeenko *et al.*, 2006) of the carbonyl dipole moments in the 4-bromobenzophenone molecule, we estimate this dipole–dipole interaction to be between 4.3 and 4.5 kJ mol^{-1} at any temperature in both polymorphs. Considering that the energy of a typical C—H···π interaction ranges from 4.2 to 20.9 kJ mol^{-1} (Desiraju, 2002) and that every molecule in both forms (*cf.* Figs. 3 and 4) has four independent C—H···π contributions from the two nearest neighbors, the carbonyl dipole–dipole interaction is not predominant. It is interesting that the short contacts between inversion-related neighbors, capable of influencing the intramolecular charge distributions, *viz.* Br···Br and C═O···C═O, differ noticeably between the polymorphs. At 100 K, the Br···Br distance is shorter (4.069 Å) in the *t*-form compared with the *m*-form (4.392 Å). The relation for the C═O···C═O distance is inversed: in the *t*-form it is larger (3.507 Å) than in the *m*-form (3.457 Å).

The data obtained for the *m*-form at three temperatures were utilized to analyze how thermal expansion affects the conformational parameters and the distances that control the

weak hydrogen bonding. In Fig. 5 we plot the temperature dependence of the four lattice parameters a, b, c and β of the m-form, all normalized to the respective values (with subscript 0) at 100 K. The thermal expansion is large and highly anisotropic; the linear thermal expansion along axis b, $\alpha_b = d\ln b(T)/dT$, is considerably larger than along c (by a factor of 3.6) or a (by a factor of 7.8). This anisotropy is quite common for all benzophenone derivatives, for instance, in 4,4′-dichlorobenzophenone (Mitkevich *et al.*, 1999) or 4,4′-dibromobenzophenone (Perić & Kojić-Prodić, 2000). The direction of the largest expansion is along the b axis, which is close to normal with respect to the plane of identically oriented molecules, like in Fig. 4. Considering the fact that the weak hydrogen bonds in the m-form operate within plane bc, we conclude that these bonds contribute essentially to the respective anharmonicities, thereby increasing the linear thermal expansion coefficients along axes b and c (*cf.* Fig. 5). The same reasoning is applicable for the similarly large thermal expansion anisotropy in 4,4′-dichlorobenzophenone.

The distances in the four available C—H$\cdots\pi$ weak hydrogen bonds in the m-form also become appreciably shorter with decreasing temperature. In Fig. 6 we show the temperature-related variation only of the shortest and longest distances in question. The points for the other two intermediate bond distances fall in between. The important torsion angles O—C1—C1$_{a(b)}$—C2$_{a(b)}$, which influence the charge distribution over the molecule, change insignificantly at lower temperatures compared with room temperature, which suggests that the bonding energy of the weak hydrogen contacts increases with decreasing temperature.

4. Conclusions

(i) Two growth techniques were employed for the preparation of 4-bromobenzophenone crystals. One of them, the sublimation method, resulted in single crystals with the monoclinic structure $P2_1/c$ first determined by Ebbinghaus *et al.* (1997). The other technique, the Bridgman–Stockbarger method, yielded a new polymorph, the structure of which at 100 K was found to be triclinic $P\overline{1}$ with the lattice parameters as given in Table 1.

(ii) The structure characteristics and the weak bonds are compared for the two polymorphic crystals studied. In both phases the predominant weak bond type is C—H$\cdots\pi$; the molecules are bound into sheets normal to the longer dimension of the molecules.

(iii) The structure data obtained for the monoclinic polymorph at three temperatures (100, 250 and 293 K) allowed us to determine how the conformational and lattice parameters vary with temperature. The large thermal expansion anisotropy is ascribed to an essential contribution of the weak hydrogen bonds to the anharmonicities of the crystal lattice.

(iv) Preliminary thermographic measurements give evidence that the metastable triclinic polymorph transforms irreversibly *via* melting to the stable monoclinic form close to the melting point of the latter.

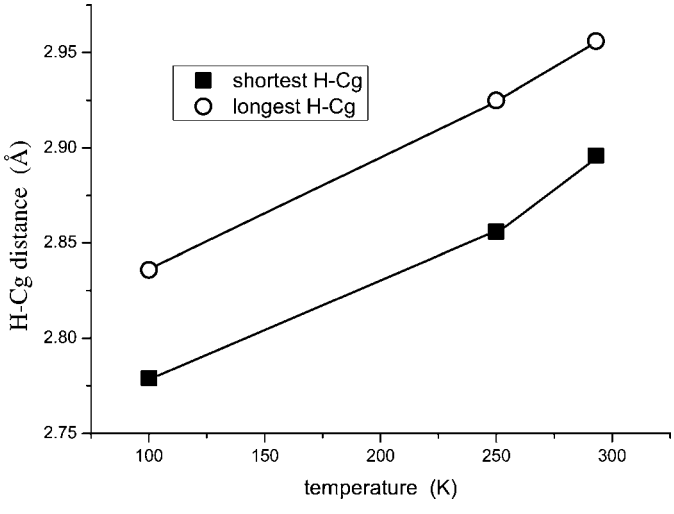


Figure 6
Distances between phenyl rings and H atoms in H$\cdots C_g$ weak bonds in monoclinic 4BrBP *versus* temperature.

The authors express sincere thanks to Alla M. Gurevich for melting temperature measurements. Helpful discussions with V. M. Koshkin are appreciated.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Avdeenko, A. A., Pyshkin, O. S., Eremenko, V. V., Strzhemechny, M. A., Buravtseva, L. M. & Romashkin, R. V. (2006). *Fiz. Nizk. Temp.* **32**, 1355–1362 (*Low Temp. Phys.* **32**, 1028–1034).
Babu, M. M. (2003). *Nucl. Acids Res.* **31**, 3345–3348.
Banga, S., Chawla, G. & Bansal, A. K. (2004). *New Trends in the Crystallization of Active Pharmaceutical Ingredients.* Pharmagenerics–2004, London, pp. 70–75.
Baumer, V. N., Romashkin, R. V., Strzhemechny, M. A., Avdeenko, A. A., Pyshkin, O. S., Zubatyuk, R. I. & Buravtseva, L. M. (2005). *Acta Cryst.* E**61**, o1170–o1172.
Bernstein, J. (2002). *Polymorphism in Molecular Crystals.* New York: Oxford University Press.
Brock, C. P., Schweizer, W. P. & Dunitz, J. D. (1991). *J. Am. Chem. Soc.* **113**, 9811–9820.
Cox, P. J., Anisuzzaman, A. T. Md., Pryce-Jones, R. H., Skellern, G. G., Florence, A. J. & Shankland, N. (1998). *Acta Cryst.* C**54**, 856–859.
Cox, P. J. & Wardell J. L. (2000). *Int. J. Pharmaceut.* **194**, 147–153.
Desiraju, G. R. (2002) *Acc. Chem. Res.* **35**, 565–573.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond.* New York: Oxford University Press.
Dvorkin, O. A., Andronati, S. A., Gifeisman, T. Sh., Simonov, Yu. O., Yavors'kii, O. S. & Pavlovs'kii, V. I. (1985). *Dopov. Ak. Nauk Ukr. SSR*, Series B, No. 8, 34–37 (in Ukrainian).
Ebbinghaus, S., Abeln, D. & Epple, M. (1997). *Z. Kristallogr.* **212**, 339–340.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gurevich, A. M. (2006). Private communication.
Lobanova, G. M. (1968). *Kristallografiya*, **13**, 984–986.
Ito, Y., Matsuura, T., Tabata, K., Meng, J.-B., Fukuyama, K., Sasaki, M. & Okada, S. (1987). *Tetrahedron*, **43**, 1307–1312.

Kutzke, H., Al-Mansour, M. & Klapper, H. (1996). *J. Mol. Struct.* **374**, 129–135.
Kutzke, H., Klapper, H., Hammond, R. B. & Roberts, K. J. (2000). *Acta Cryst.* B**56**, 486–496.
McGhie, A. R., Garito, A. F. & Heeger, A. J. (1974). *J. Cryst. Growth*, **22**, 295–297.
Mitkevich, V. V., Lirtsman, V. G., Strzhemechny, M. A., Avdeenko, A. A. & Eremenko, V. V. (1999). *Acta Cryst.* B**55**, 799–806.
Mullin, J. W. (2001). *Crystallization*, 4th ed. Woburn: Butterworth Heinemann.
Nangia, A. (2002). *Cryst. Eng. Commun.* **17**, 1–9.
Oxford Diffraction (2005). *CrysAlis*, Release 1.171.26. Oxford Diffraction Ltd, Oxford, UK.
Perić, B. & Kojić-Prodić, B. (2000). *Acta Cryst.* C**56**, 211–212.
Scheel, H. J. (2003). *Crystal Growth Technology*, edited by H. J. Scheel & T. Fukuda, pp. 3–14. Chichester, New York: John Wiley and Sons.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97, Release 97-2. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Turro, N. J. (1992). *Modern Molecular Photochemistry*, ch. 9. Herndon, VA: University Science Books.
Weast C. R. (1986). Editor. *CRC Handbook of Chemistry and Physics*, 66th ed., p. C-138. Boca Raton: CRC Press.
Zhan, B., Lu, W.-Q., Zhou, Z.-H. & Wu, Y. (2000). *J. Mater. Sci.* **10**, 1513–1517.
Zhang, Y., Wu, G., Wenner, B. R., Bright, F. V. & Coppens, P. (1999). *Cryst. Engng*, **2**, 1–8.
Zúñiga, F. J. & Criado, A. (1995). *Acta Cryst.* B**51**, 880–888.