



Discovery of a new polymorphic phase of ortho-bromobenzophenone



J. Baran^a, N.A. Davydova^{b,*}, M. Drozd^a

^a Institute of Low Temperature and Structure Research, PAS, 50-950 Wrocław, Poland

^b Institute of Physics, NANU 46 pr. Nauki, 03028 Kiev, Ukraine

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ABSTRACT

We present the first experimental spectroscopy and calorimetry proof of the existence of polymorphism in ortho-bromobenzophenone (2BrBP). The crystallization and melting processes of the two polymorphic phases were monitored by infrared spectroscopy. The crystallization of the metastable phase occurs in the supercooled region at 245 K upon heating of the glassy 2BrBP. The metastable phase melts below the stable phase, i.e. at 301.0 K. After melting of the metastable phase it is transformed into a stable phase at room temperature. The stable polymorph melts at 316.5 K.

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1. Introduction

Benzophenones are compounds of great scientific and applied interest due to the varied physicochemical properties, that they possess. Several benzophenones are widely used in nonlinear optics [1–5], in light-emitting diodes [6] and in optoelectronics [7].

The molecule structure of benzophenone is influenced by the steric interaction of the two *ortho* H atoms that distort the planarity of the aromatic ring and carbonyl group. Traditionally, the symmetry of the molecule is characterized by two torsion angles between the averaged planes of the rings and the carbonyl group.

We reported in 2006 by the measurements of Fourier transform infrared (FT-IR) spectroscopy and calorimetry that the substitution site within the same aromatic ring (*ortho* or *para*) plays a crucial role in the physical properties of bromo substituted benzophenones: 2-bromobenzophenone and 4-bromobenzophenone (2BrBP or 4BrBP, correspondingly) [8]. Br atom in an *ortho* position determines excellent glass-forming ability with a wide supercooled liquid temperature region, and high thermal stability against crystallization of 2BrBP. However, the Br atom in a *para* position shows an opposite behavior. 4BrBP readily crystallizes on cooling, even for high cooling rates. Such behavior is a result of the geometrical structure of the molecules. Substitution at the *ortho*-position results in a large asymmetry of the molecule, which is result of the conjugation of the substituted aromatic ring with the C=O bond. The torsion angle involving atoms of the substituted aromatic ring in 2BrBP is unusually large (-68.3°), especially compared with the torsion angle of the unsubstituted aromatic ring (-17.6°) [9]. These

torsion angles are different from that of 4BrBP, where the molecule is slightly asymmetric (the above mentioned angles are -21.6° and -28.1°) [10]. The important role of the bromo group in improving the nonlinear properties of organic materials was reported by B. Zhao et al. [7]. Namely it was shown that the bromo group is an effective group for microscopic and macroscopic second-order nonlinearities, and can also improve the transparency and the thermal stability of the compounds. On the other hand, the possibility of the metastable phase formation in the compounds can lead to uncontrolled instability that has dramatic consequence.

Up to now, the only one crystallographic form for 2BrBP is known, which has a monoclinic $P2_1/a$ space group [9]. At the same time benzophenone and 4BrBP are known to exist under two polymorphic phases [10,11]. Considering the importance of bromo-substituted benzophenones for industrial applications the search for new polymorphic modification of 2BrBP is of interest.

In the present work we report the discovery of a new polymorphic modification of 2BrBP by applying FT-IR spectroscopy and differential scanning calorimetry (DSC). Both methods will allow us to locate the preferred temperature regions of growth for the two polymorphic modifications and to determine the crystallization and melting temperatures of the new polymorph.

2. Experimental

2BrBP purchased from Factory of Chemical Reactants in Shostka (Ukraine) was purified first by multiple recrystallization from ethanol solution and then by absorption chromatography using aluminum oxide.

Infrared measurements were done on Fourier-transform infrared spectrometer (Bruker model IFS-88) at a resolution 2 cm^{-1} and 32 scan were typically co-added for an individual spectrum

* Corresponding author.

E-mail address: Davydova@iop.kiev.ua (N.A. Davydova).

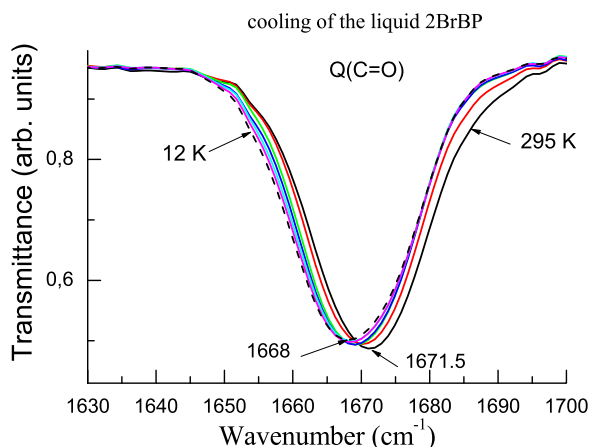


Figure 1. Temperature-dependent FT-IR spectra for liquid 2BrBP in the C=O stretching vibration region recorded on cooling. Temperatures are (from right to left): 295, 250, 200, 150, 70, and 12 K.

in the frequency range 400–4000 cm^{-1} . Data processing was performed with OPUS software. For the FT-IR measurements, a sample of powder 2BrBP was inserted in a cell with two CsI pellets at room temperature and then melted into a thin film. The thickness of such a cell was approximately a few micrometers. Such a sample with liquid 2BrBP was then fixed in an Oxford Duplex closed-cycle cryostat that can be operated in the temperature range 330–12 K with an accuracy of roughly 1 K.

DSC measurements were made by a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with the CCA-7 low temperature accessory. Liquid nitrogen was used as a coolant and the measurements were carried out in the temperature range 104 up to 343 K. A small amount of the sample was enclosed in aluminum pans hermetically sealed with the use of a sample encapsulating press. Temperatures and enthalpies were calibrated using Indium.

3. Results

3.1. Infrared spectra

Before discussing the results we wish to note that 2BrBP molecules are involved in the formation of an intermolecular hydrogen bonding of C–H...O=C and C–H... π types in which molecules interact via weak non-directional van der Waals forces [9]. We have studied FT-IR transmission spectra in the 400–4000 cm^{-1} spectral range. However, in this study, processes of vitrification and crystallization we will monitor by following changes in the shape and position of the characteristic C=O stretching band in the 1630–1700 cm^{-1} spectral range, for which the maximal influence of the structural changes should be expected.

At first, the powder crystalline sample was melted. The liquid sample was then cooled down through the glass transition ($T_g = 224.8$ K) to 12 K and the FT-IR spectra were recorded on cooling (Figure 1). It is clear from Figure 1 that the shape of the C=O band during transformation from the liquid to glass state are almost unchanged. Only a little gradual low-frequency shift of the position of the C=O band from 1671.7 to 1668 cm^{-1} with decreasing temperature is observed. This means that, during cooling, the crystallization of the liquid state is avoided.

On the subsequent heating from the glass state to room temperature, the crystallization occurs. We analyzed the structural evolution during crystallization in real time by continuously measuring the FT-IR spectra during isothermal aging performed at 295 K (Figure 2). The solid curve (0 min) corresponds to the initial FT-IR

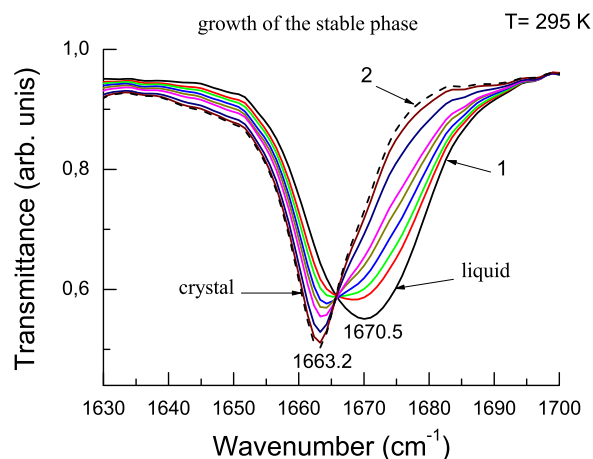


Figure 2. Evolution of the FT-IR spectra of 2BrBP during crystallization of the stable phase at 295 K in the C=O stretching vibration region. The solid curve (1) corresponds to the initial spectrum of the liquid state. The next spectra were recorded each 7 min (7, 14, 21, 28, 35, 42, 49, and 56 min) after recording the spectrum 1. The dash curve (2) corresponds to the spectrum of the stable crystal.

spectrum of the liquid state. The next spectra were recorded each 7 min (7, 14, 21, 28, 35, 42, 49, and 56 min) after recording the initial spectrum. It is seen that the transformation associated with the crystallization process is completed within 56 min (Figure 2, dash curve). The crystallization is accompanied by a narrowing of the wide C=O band in the liquid phase (solid curve in Figure 2) and the shift of the band by ~ 7.3 cm^{-1} to the position 1663.2 cm^{-1} in the crystal state (dash curve in Figure 2). No changes in the spectra were observed after 56 min.

To obtain a new polymorphic modification of 2BrBP (thereafter will be called metastable), we used another thermal procedure. This time we first cooled the liquid sample from room temperature through the glass transition to 100 K, and then the glassy sample was heated to 245 K and kept at this temperature. During heating from 100 to 245 K the temperature dependent FT-IR spectra were recorded (Figure 3). It is seen that with increasing temperature the spectra of the glassy and liquid states in the temperature range 100–245 K practically do not differ from each other, only a small shift by ~ 2 cm^{-1} to the higher frequencies is seen. However when the supercooled liquid sample was kept at 245 K for 60 (Figure 3, curve 2) and 75 min (Figure 3, curve 3) significant changes were observed in the spectrum associated with the crystallization.

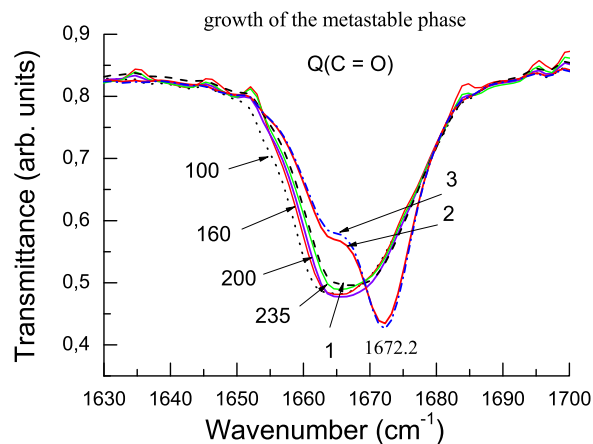


Figure 3. Temperature-dependent FT-IR spectra for 2BrBP in the C=O stretching vibration region recorded on heating from 100 to 245 K (curve 1). The dash curve (1) corresponds to the spectrum at 245 K. The next spectra 2 and 3 were recorded since 60 min and 75 min after recording the spectrum 1.

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