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Metastable β-phase of benzophenone: independent structure determinations *via* X-ray powder diffraction and single crystal studies

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Benzophenone was the first organic molecular material to be identified as polymorphic. It is well known that benzophenone crystallizes in a stable orthorhombic α-form (m.p. 321 K) with space group $P2_12_12_1$ and a = 10.28, b = 12.12, c = 7.99 Å, [Girdwood (1998). Ph.D. thesis. Strathclyde University, Glasgow, Scotland]. Here we report two separate structure determinations of the metastable β-form (m.p. 297–299 K). Crystalline material of the metastable polymorph was obtained from a melt supercooled to ~243 K. The structure was determined from X-ray powder diffraction data by employing a novel, computational systematic search procedure to identify trial packing arrangements for subsequent refinement. Unit-cell and space-group information, determined from indexing the powder diffraction data, was used to define the search space. The structure was also determined from single-crystal diffraction data at room temperature and at 223 K. The metastable phase is monoclinic with space group $C2/c$ and a = 16.22, b = 8.15, c = 16.33 Å, β = 112.91° (at 223 K). The structures derived from the individual techniques are qualitatively the same. They are compared both with each other and with the stable polymorph and other benzophenone derivatives.

1. Introduction

Benzophenone crystallizes in two polymorphic forms with melting points 321 K (stable phase) and 297–299 K (metastable phase; Groth, 1919). The structure of the stable phase was first determined by Vul & Lobanova (1967), Lobanova (1968), Fleischer *et al.* (1968) and Girdwood (1998). The structure is orthorhombic with space group $P2_12_12_1$ and cell parameters a = 10.28, b = 12.12, c = 7.99 Å (Girdwood, 1998). The existence of a monoclinic metastable phase was recognized as early as 1871 and was the object of many early crystallization studies. However, no structural data have been published up to now. In addition to the data collected at 223 K for the metastable phase of benzophenone, the structure of the stable phase was also determined at 223 K to allow a better comparison of the molecular packing of the stable and metastable modifications.

Despite considerable experimental endeavour, attempts to grow a single crystal of the metastable phase suitable for structure analysis were initially unsuccessful. Hence, the metastable phase of benzophenone was regarded as an ideal test case with which to evaluate a new method for determining crystal structures from X-ray data derived from microcrystalline powders. Although a single-crystal structure was subsequently obtained, the two methods of structure determination were carried out quite independently. It is empha-

sized that this study was a test of a new methodology and the determination from powder data should be considered on its own merits. In the absence of a single-crystal structure, as was anticipated in this case, the benefit of having an alternative approach for structure determination is clear and full details of the method of determination from the powder data are therefore presented here. Given the historical importance of benzophenone in the study of the polymorphism of molecular materials, the present work is first placed in its historical context.

2. Historical background[1]

Benzophenone crystallizes in a stable orthorhombic α-form and a metastable monoclinic β-form (Groth, 1919). Although some very early reports may indicate the occurrence of polymorphism in organic crystals (*e.g.* Woehler & Liebig, 1832; Laurent, 1842), the metastable phase of benzophenone was the first clearly observed polymorphic form of an organic molecular crystal (Gossner, 1904). Today polymorphism is well known as a widespread property of organic materials but, in the days of its first observation, it seemed to be a mysterious phenomenon observed for only a few substances and hence gave rise to significant research activity, much of which has been forgotten.

Metastable benzophenone was first prepared and described by Zincke (1871) in Bonn and became the most studied organic polymorph around the turn of the century (*e.g.* Lehmann, 1877; Tanatar, 1892). A contemporary overview of the early theories on polymorphism involving benzophenone was given by Gossner (1904) and later a brief survey of the historical development of polymorphic concepts by Buerger & Bloom (1937). Although metastable β-benzophenone was the object of intense interest, descriptions of the growth, morphology, quality and properties of the crystals were rather vague and partly contradictory. The only observation noted at that time was the formation of 'monoclinic prisms with a pinacoid' (Prendel, 1892) and this was from a visual inspection without any measurement of the interfacial angles. The melting point of metastable benzophenone was found to be 297–299 K, *i.e.* much lower than the melting point of the orthorhombic stable modification, m.p. 321 K.

The formation of the metastable phase and its transformation into the stable phase were mainly studied by Schaum (*e.g.* Schaum, 1897; Schaum & Schoenbeck, 1902), who obtained the metastable phase *via* crystallization from the supercooled melt. The transformation into the stable phase is monotropic and destructive, and can be initiated by mechanical load or contact with the stable phase. Frequently it occurs spontaneously. There are no conditions known under which the β-form is more stable than the α-form. With regard to the formation of the two different phases, Schaum's ideas changed with time. The nucleation of the metastable phase seemed to be facilitated by prior heating of the melt to $\sim$423 K. His final conclusion was that, during this pre-treatment of the melt, the molecules change their shapes from an α- into a β-form. During supercooling of the melt, the β-form of the molecules was assumed to be preserved and to induce the nucleation of the metastable phase. In addition, it was found that the β-form molecules could easily transform back into the stable α-form and thus it was assumed that the metastable crystals, which transformed spontaneously, must contain a small amount of α-form molecules. Since, at that time, the nature of the transformation was not clear, Schaum (1914) called the phenomenon 'cryptochemical polymorphism'. After this time interest in metastable benzophenone decreased and it could be described as a 'disappearing polymorph' (Dunitz & Bernstein, 1995). Later works do not concern crystal growth or structure determination, but focus on solidification or spectroscopic and thermodynamic aspects.

Melnik *et al.* (1980) found that pre-treatment of the melt appeared to have no significant influence on the nucleation of either phase and that nucleation of the metastable phase simply required a supercooling of the melt down to a temperature in the range 238–248 K. At higher temperatures than this nucleation of the stable phase is favoured. At lower temperatures the metastable phase was found not to nucleate so easily, whilst below 203 K it has been suggested that a glassy phase, γ-benzophenone, exists. Recently, Graham *et al.* (1995), who broadly confirmed the results of the previous studies, investigated the formation of these different polymorphic modifications and developed a model of the solidification process.

The increasing importance of polymorphism in organic materials (see *e.g.* Bernstein, 1993) provides a stimulus to complement these previous investigations *via* a detailed crystallographic analysis of the metastable β-polymorph.

3. Powder diffraction study

3.1. Preparation of powder sample

The metastable phase was grown *in situ* within a 1 mm diameter capillary. Powder of the stable α-phase was placed within the capillary, melted and heated up to $\sim$373 K. After cooling to room temperature, the capillary was mounted and aligned on a goniometer head fixed onto the axis of a Siemens D5000 powder diffractometer equipped with an Oxford Instruments CRYOSTREAM nitrogen flow cooling attachment. The sample containing the supercooled melt was cooled to a temperature of 243 K and after a few hours the polycrystalline metastable β-phase had formed.

3.2. X-ray powder data collection

The D5000 diffractometer was equipped with a focusing Ge primary beam monochromator, linear position-sensitive detector and Cu $K\alpha$ incident radiation. The sample was rotated about the capillary axis and X-ray diffraction data were collected in transmission mode over the 2θ range 5–60° with an equivalent step size of $2\theta = 0.016°$. The total data acquisition time was 6 h. Silicon powder was used as an external calibration standard. A sample temperature of 285 ±

[1] For an extended list of historical papers please contact the authors.

0.2 K was maintained throughout the period of data acquisition.

3.3. Identification of unit cell and space group from powder data

Diffraction peak positions were identified and refined *via* peak fitting using a pseudo-Voigt function and indexed using the computer programs *ITO* (Visser, 1969) and *DICVOL* (Boultif & Louer, 1991) by examining the 2θ positions of the first 20 reflections in both cases. The unit-cell parameters obtained from the powder diffraction data, and subsequently refined during the Rietveld refinement procedure, are detailed in Table 1. Consideration of the systematic absences in the diffraction pattern led to the choice of likely space groups as either *Cc* or *C*2/*c*. Recognizing that the unit-cell volume was consistent with the presence of eight benzophenone molecules, the space group was taken as *C*2/*c* on the working assumption that there were unlikely to be two molecules in the asymmetric unit.

3.4. Computational method for evaluating trial structures

Following pattern indexing and space-group identification, the key step in structure determination from powder data is the reliable generation of trial packing motifs in the postulated unit cell. This study employed a systematic search method (Hammond *et al.*, 1997) to generate packing motifs from a grid-based search in direct space, performed in the context of a predetermined unit cell. The searches treat molecular rotations and translations and, where appropriate, conformational variations, to locate trial structures. Structures are selected according to cut-off criteria that define the minimum allowed separation between atoms in adjacent molecules. The selected structures are ranked using calculated lattice energies and *via* a comparison between calculated and experimental powder X-ray data.

As part of the validation of the methodology of Hammond *et al.* (1997), a systematic search was performed using the cell parameters and space group for the stable form of benzophenone in an attempt to reproduce the experimentally observed packing arrangement. The two torsion angles describing the orientation of the phenyl moieties were included as variables in the search space. The method correctly identified the experimentally observed molecular packing in the stable phase of benzophenone; *i.e.* the structure was ranked as the best structure evaluated in terms of calculated lattice energy, without employing lattice energy minimization. This demonstrated the validity of this approach for trial structure generation.

3.5. Application to metastable benzophenone

To perform the systematic search for trial structures it was first necessary to derive a molecular model for benzophenone. As a starting point here, the molecular geometry was taken from a recent single-crystal structure determination of the stable α-phase (Girdwood, 1998), but in the general case single-crystal data may not be available as a point of reference.

Table 1
Crystallographic details for the powder determination of the metastable phase of benzophenone.

Cell parameter	Metastable phase (determination from powder at 285 K)
a (Å)	16.222 (1)
b (Å)	8.147 (3)
c (Å)	16.334 (1)
α (°)	90.0
β (°)	112.911 (5)
γ (°)	90.0
Space group	*C*2/*c*
Z	8
Cell volume (Å^3)	1988.35 (13)
Density (g cm^{-3})	1.218

The semi-empirical molecular orbital program *MOPAC* (Stewart, 1990) provides a quick computational method for deriving a molecular model. As this study was intended as an objective test of a methodology for determining crystal structures from powder data, it was decided to optimize the molecular geometry taken from the single-crystal determination with *MOPAC* using the AM1 method. The keywords PRECISE (convergence criteria stringency increased 100 times) and EF (eigenvector following) were specified in the optimization procedure.

The most significant difference between the molecular geometries derived, respectively, from *MOPAC* and the crystal structure of the stable phase is in the positions of the H atoms. This is to be expected as, for *MOPAC*, C—H bond lengths are parameterized from neutron diffraction data and reflect the internuclear separations, whereas the H atoms are positioned from maxima in the electron density distribution in X-ray studies yielding consistently shorter bond lengths. The calculated point charges used in the systematic search have been deposited as supplementary material.[2]

The fully optimized *MOPAC* AM1 geometry, with the associated point charges, was employed as the probe molecule in the systematic search. Initially, an energy screen of possible molecular conformations of an isolated molecule was performed. The conformations were explored using two independent torsion angles, C9—C8—C1—O1 and O1—C1—C2—C3 (Fig. 1). Both torsion angles were examined in 10° steps in the range 0–170°.

All conformations within an energy window of 10.5 kJ mol^{-1}, with respect to the global minimum, were accepted for consideration in the subsequent systematic search. A total of 80 separate conformations were selected on this basis. The intramolecular energy terms included in the calculation of conformational energies were van der Waals and Coulombic non-bonded interaction terms and a specific torsion energy term; full details are given elsewhere (Mayo *et al.*, 1990). All nearest-neighbour interactions up to and

[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0561). Services for accessing these data are described at the back of the journal.

Table 2
Parameter values employed in the systematic search for trial packing motifs for the metastable phase of benzophenone.

Search parameter	Range of values	Increment employed
Rotation about *a* axis (°)	0–350	10
Rotation about *b* axis (°)	0–350	10
Rotation about *c* axis (°)	0–350	10
Translation along *a* axis (fractional)	0.0–0.45	0.05
Translation along *b* axis (fractional)	0.0–0.45	0.05
Translation along *c* axis (fractional)	0.0–0.45	0.05
Torsion angle C3—C2—C1—O1 (°)	0–170	10
Torsion angle O1—C1—C8—C9 (°)	0–170	10

Table 3
Summary of results of the systematic search for trial packing motifs for the metastable phase of benzophenone.

Total number of configurations tried	3.732×10^9
Configurations eliminated without explicit testing	3.347×10^9
Total number of failed configurations	3.8581×10^8
Failures on non-bonded distance criteria	3.8580×10^8
Failures on lattice energy criteria	4420
Failures on X-ray powder diffraction fit criteria	4201
Failures on both energy and diffraction fit criteria	4172
Successful configurations on lattice energy	132
Successful configurations on diffraction fit	351
Total successful configurations	380

including level 1 to level 4 interactions were excluded from the intramolecular energy summation.

Clearly, calculated atomic point charges are a function of molecular geometry. However, the use of an invariant set of charges for all molecular conformations within the systematic search was considered to be reasonable as, in this case, the magnitudes of the changes, evaluated for various molecular conformations, were found to be small.

The search parameters employed in the execution of the systematic search program, given in Table 2, included a distance cut-off of 2.1 Å and lattice energy cut-off of -42 kJ mol^{-1}. The calculated $R_{\rm wp}$ fit factor is given by

$$R_{\rm wp} = \left[\sum_{i=1}^{n} w_i (Y_{i\rm obs} - \lambda y_{i\rm calc})^2 / \sum_{i=1}^{n} w_i Y_{i\rm obs}^2 \right]^{1/2}. \qquad (1)$$

Here $y_{i\rm obs}$ and $y_{i\rm calc}$ are the observed and calculated profile intensities, λ is the calculated scale factor for the best fit and w_i the profile point weighting factor, here taken as $1/y_{i\rm obs}$.

The lattice energies were calculated using the parameters for non-bonding interactions from the Dreiding potential (Mayo *et al.*, 1990). The use of these parameters was considered desirable for consistency with the method used to calculate torsion energies. The differential intramolecular energies associated with particular conformations (energy difference calculated with respect to the most stable conformation) were added as energy penalties to yield overall calculated lattice energies.

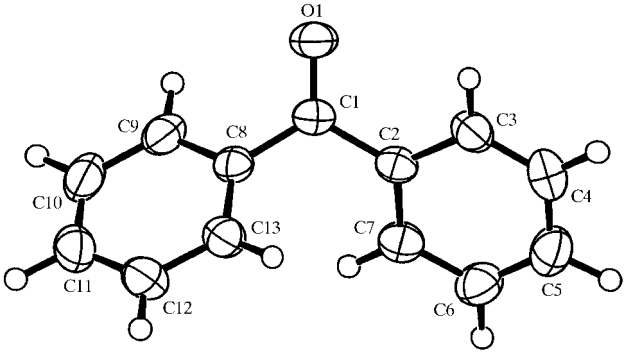


Figure 1
*ORTEP*II (Johnson, 1976) plot of a molecule of metastable benzophenone at 223 K showing the atom numbering employed throughout.

The results of the ranking procedure for trial structures are summarized in Table 3. Of the 3.73 billion separate packing arrangements in the search path (much fewer actually needing to be explicitly examined), only 132 were found to be acceptable in terms of the calculated lattice energy and 351 acceptable in terms of the fit of the diffraction data. In this instance the best trial structure in terms of lattice energy was also found to be first in the ranking of the $R_{\rm wp}$ fit of the diffraction profiles.

The best trial structure from the systematic search was taken for progression to a final structure determination *via* Rietveld (1969) refinement. For the purposes of comparing the use of similar but different starting positions in the Rietveld refinement procedure, the best trial structure was optimized using the Crystal Packer module of the *Cerius*^{2} molecular modelling package (Molecular Simulations Inc., 1998). Two separate calculations were made without relaxation of the unit-cell parameters:

(i) optimization allowing only rigid-body rotations and translations, and

(ii) optimization allowing, in addition, subrotations about the two torsion angles specified in the systematic search.

3.6. Rietveld refinement

Rietveld refinement is most frequently applied to inorganic systems in which the atoms are not restrained within molecular assemblies. As a result, existing refinement methods are not ideal for treating organic molecular materials. Structure refinement was carried out using the Rietveld refinement program *GSAS* (Larson & Von Dreele, 1985). Initially a model-free Le Bail fit (Le Bail, 1988) was used to determine the model, independent parameters describing background scattering and line shape.

The three initial models considered for refinement were:

(i) best trial structure before optimization with respect to lattice energy;

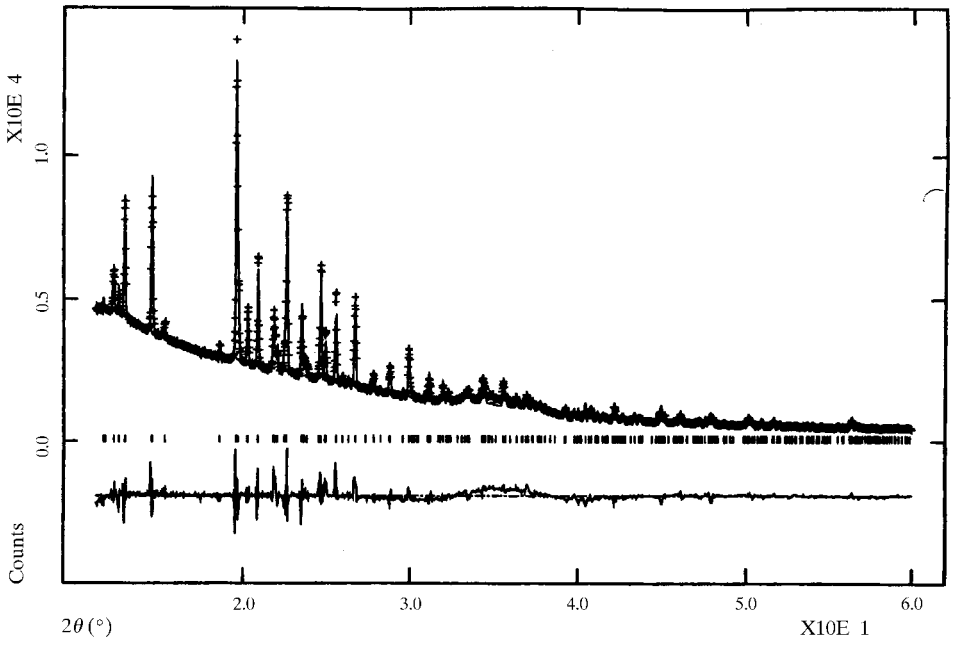
(ii) best trial structure after optimization as a rigid body;

(iii) best trial structure after further relaxation of the torsion angles.

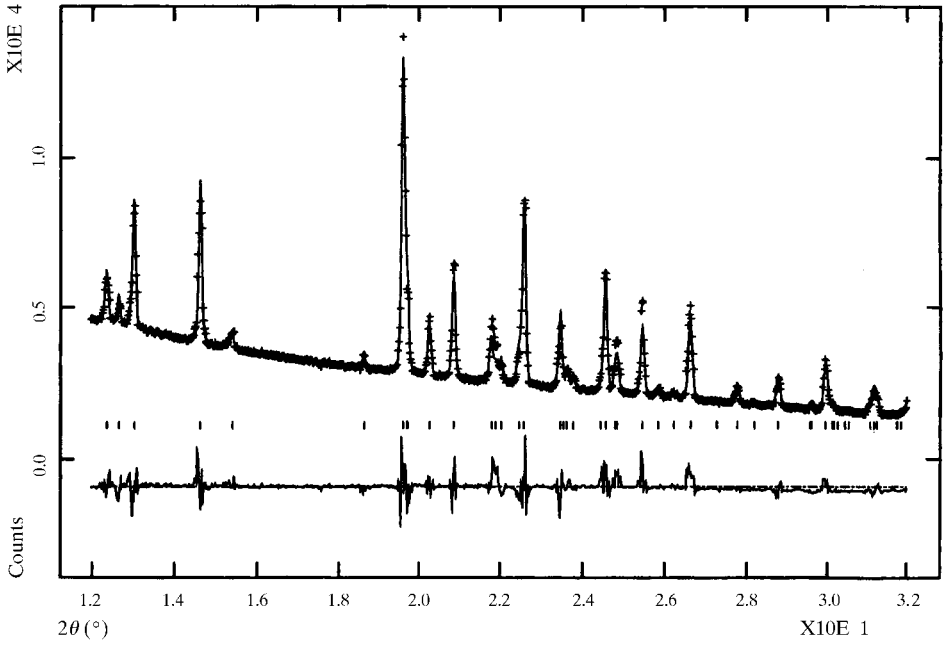
Model (iii) gave the best fit to the diffraction data prior to any relaxation of the atomic positions and was therefore progressed for rigid-body refinement. The residuals R_p of the

initial fit were 0.055 and the weighted residuals R_{wp} were 0.083. This initial fit is quite satisfactory and so the associated fractional coordinates are provided as supplementary material for deposition (see footnote **2**).

During the subsequent refinement procedure, rigid bodies were defined to maintain the two phenyl groups in a planar configuration, and to describe the position and orientation of the carbonyl group. The three rigid bodies were defined with a common origin. The orientations of the rigid bodies, describing the phenyl moieties, were allowed to refine independently with respect to rotations about their pseudo-twofold axes in the phenyl planes (C2—C5 and C8—C11, respectively) and axes normal to each phenyl plane through the origin. In the rigid-body description of the phenyl rings a unique C(ar)—C(ar) bond length parameter was refined. The separation of the atoms in the carbonyl group was also varied during the refinement. By using rigid-body definitions, just 13 independent parameters were used to describe the positions of the atoms during the refinement, when it became clear that the diffraction data could not, justifiably, be used to support a more detailed model of the structure.



Complete powder profile and Rietveld refined model.



Detail of region between 12 and 32° 2θ

Figure 2
Comparison of the Rietveld refined model and experimental X-ray diffraction profiles together with a difference plot for metastable benzophenone.

The final model fit to the experimental diffraction data and a difference plot are given in Fig. 2. The residuals R_p of the final fit were 0.047 and the weighted residuals R_{wp} were 0.069. The fractional coordinates of the non-H atoms and their standard deviations are given in Table 4. The most significant bond lengths, bond angles and torsion angles are given in Table 5. It should be noted that when, for the final refined structure, the rigid-body formalism was replaced by soft distance constraints and the refinement was continued, a severely distorted molecular geometry resulted. The only significant difference between the initial and final Rietveld refined structures is the angle between the planes of the phenyl rings. The angle in the trial structure, based on a lattice energy optimization, is 70.6°, whereas the angle is 65.2° in the final refined structure.

4. Single crystal study

4.1. Preparation of single crystals

The crystal growth and morphology of the stable modification of benzophenone have been studied under various growth conditions (*e.g.* Linnemann, 1865; Wickel, 1886; Nacken, 1915; Bleay *et al.*, 1978; Roberts *et al.*, 1993; Borisov, 1993). As outlined above, there is very little published infor-

Table 4
Fractional coordinates of non-H atoms in the asymmetric unit of the metastable phase of benzophenone as found after Rietveld refinement.

	x	*y*	*z*
O1	0.3802 (6)	0.1508 (22)	0.9751 (12)
C1	0.3784 (6)	0.2424 (20)	0.9228 (5)
C2	0.4685 (7)	0.3183 (11)	0.9157 (5)
C3	0.5480 (8)	0.2240 (13)	0.9436 (8)
C4	0.6261 (8)	0.2898 (18)	0.9375 (7)
C5	0.6248 (9)	0.4500 (18)	0.9033 (5)
C6	0.5453 (10)	0.5443 (16)	0.8754 (9)
C7	0.4671 (9)	0.4785 (14)	0.8816 (8)
C8	0.2910 (8)	0.2968 (11)	0.8547 (7)
C9	0.2211 (7)	0.3455 (16)	0.8809 (7)
C10	0.1380 (8)	0.3972 (16)	0.8161 (6)
C11	0.1247 (7)	0.4002 (15)	0.7252 (7)
C12	0.1947 (7)	0.3515 (18)	0.6990 (7)
C13	0.2778 (7)	0.2998 (16)	0.7638 (7)

mation about the crystal growth of the metastable phase and so our study started with attempts to reconstruct the old recipes. The following procedure to prepare the metastable phase leads, finally, to reproducible results. Stable benzophenone (Aldrich, Merck) was melted in a sealed glass ampoule, heated to 373–423 K for a few hours and then supercooled down to a temperature between 238 and 248 K. After a few minutes the metastable β-phase nucleated spontaneously. At higher temperatures nucleation of the stable α-phase is favoured. At temperatures below 228 K neither nucleation nor crystal growth was observed. In accordance with Melnik *et al.*'s (1980) findings, pre-heating the melt had no influence on the nucleation of the metastable phase. The only crucial parameter for nucleation of the metastable phase is the temperature of the melt, which should be kept between 238 and 248 K.

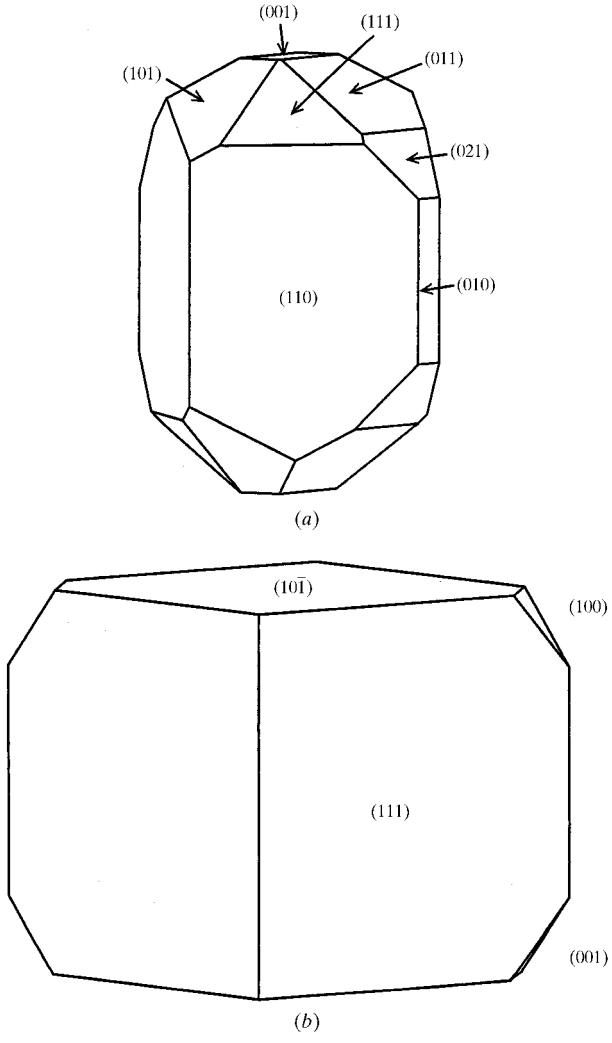


Figure 3
Typical morphologies of (*a*) orthorhombic stable and (*b*) monoclinic metastable benzophenone polymorphs.

Table 5
Molecular geometry (Å, °) of the metastable phase of benzophenone after Rietveld refinement of the best trial structure obtained from the systematic search procedure.

Bond definition	
C1—C2	1.63 (1)
C1—C8	1.49 (1)
All C—C in phenyl moieties	1.42 (1)
C1—O2	1.13 (2)
Bond angle definition	
C2—C1—C8	116.9 (4)
C2—C1—O1	123.1 (2)
C8—C1—O1	120.0 (3)
Torsion angle definition	
C3—C2—C1—O1	30.0
O1—C1—C8—C9	47.6
Angle between the planes of the phenyl moieties	
	65.2

Grains of polycrystalline material (m.p. 297–299 K) were placed into benzophenone melt slightly supercooled with respect to the metastable phase, *i.e.* at 296–298 K. The grains grew on a timescale from 30 min to a few hours forming intergrown crystals up to a few millimeters in diameter. From these aggregates single-crystal seeds for the growth of large crystals were cut using a razor blade. During this procedure the crystals and tools were cooled in order to prevent the destructive transformation into the stable phase. The growth experiments were performed in a temperature-controlled air chamber. In a melt supercooled by ~0.1–0.3 K below the melting point of β-benzophenone, large single crystals of 1–2 cm edge lengths were obtained within 1–2 d.

In contrast to the rich morphology of the stable form (Fig. 3*a*), metastable benzophenone develops the monoclinic prism {111} and the pinacoid {10$\bar{1}$}. Larger crystals may also show the pinacoids {100} and {001} (Fig. 3*b*).

4.2. Single-crystal structure determination

Diffraction data for metastable benzophenone were recorded at room temperature and 223 K. All measurements were carried out on a Rigaku AFC-6*R* four-circle diffractometer equipped with a cold stream device. Mo $K\alpha$ radiation and a graphite monochromator were used. Data reduction was

Table 6
Crystal data and details of the single-crystal measurements of the stable and metastable phase of benzophenone at different temperatures.

	Stable form, 293 K (Girdwood, 1998)	Stable form, 223 K (Kutzke, unpublished)	Metastable form, 293 K (this work)	Metastable form, 223 K (this work)
Molecular formula	$C_{13}H_{10}O$	$C_{13}H_{10}O$	$C_{13}H_{10}O$	$C_{13}H_{10}O$
Molecular weight	182.22	182.22	182.22	182.22
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$	$C2/c$
a (Å)	10.281 (3)	10.270 (1)	16.232 (5)	16.200 (4)
b (Å)	12.123 (3)	12.090 (5)	8.163 (2)	8.104 (1)
c (Å)	7.987 (1)	7.905 (3)	16.362 (5)	16.248 (4)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	112.94 (2)	112.82 (2)
γ (°)	90.00	90.00	90.00	90.00
Unit-cell volume (Å^3)	995.44 (4)	981.52 (0.5)	1996.54 (1.1)	1966.17 (0.74)
Volume per molecule	248.86	245.38	249.57	245.77
D_c (g cm^{-3})	1.216	1.233	1.212	1.231
Z	4	4	8	8
No. of independent reflections	1235	1172	519	1144
No. of refined variables	138	167	167	167
S	2.44	1.873	7.040	2.383
Shift/error	0.00	0.000	0.232	0.041
$2\theta_{max}$ (°)	53	60	35	50
R_{int} (%)		2.4	4.2	4.0
R/wR	0.049/0.070	0.038/0.029	0.070/0.064	0.035/0.035

carried out using Lorentz and polarization corrections, but neglecting absorption and extinction effects. The structures were solved by direct methods. Full-matrix least-squares refinement on F for all data was performed for the non-H atoms. The atomic displacement parameters of the H atoms were refined isotropically. All calculations were performed using the program package *TEXSAN* (Molecular Structure Corporation, 1989).

The room-temperature measurement was made close to the melting point (297–299 K) so in this case the Debye–Waller factor was high. Most of the reflection intensities from the room-temperature measurement above the diffraction angle 2θ 35° were less than three times the standard deviation above background level. Consequently, the data collection was carried out up to 2θ 35°, leading to 519 independent reflections with sufficient intensity. Moreover, the structure refinement led to inappropriate isotropic atomic displacement parameters for the H atoms and to a rather poor R value. For the data collection at 223 K, however, reflections up to 2θ 50° (1144 independent reflections) were measured and reasonable thermal coefficients were obtained for all atoms, including the H atoms.

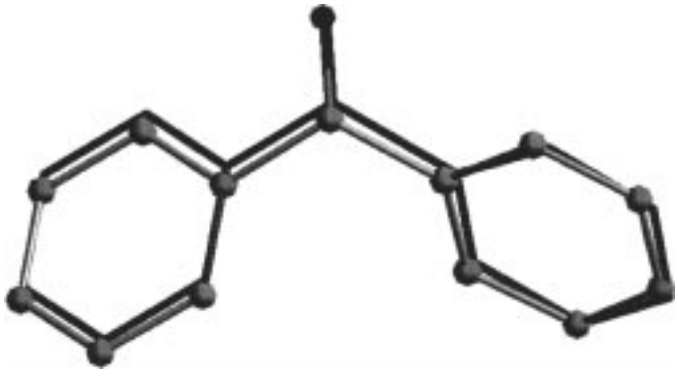


Figure 4
Comparison of molecular structures of metastable benzophenone obtained separately from single-crystal (ball-and-stick) and powder data.

5. Discussion

The single-crystal data obtained at both room temperature and 223 K for metastable benzophenone are detailed in Table 6, together with similar data for the stable phase at room temperature (Girdwood, 1998) and at 223 K (Kutzke, unpublished work). The fractional atomic coordinates and isotropic displacement parameters for the single-crystal determination of the metastable phase at 223 K are given in Table 7. Some key aspects of the molecular geometry for both the stable and metastable modifications of benzophenone are summarized in Table 8. The variation in the internal geometry of the phenyl moieties between the two phases is minimal.

5.1. Comparison of structures from single-crystal and powder data

The molecular structures determined by the two methods are shown superimposed in Fig. 4. Apart from small differences in molecular geometry, the packing arrangements are the same for both determinations. Root mean square (r.m.s.) fits over the Cartesian coordinates of the non-H atoms in the asymmetric unit from the powder and single-crystal methods gave an r.m.s. value of 0.189 ± 0.008 Å. For comparison, the r.m.s. fit for the best trial structure [model (iii)] with the single-crystal structure is 0.131 ± 0.011 Å.

5.2. Comparison of structures of the stable and metastable phases determined by single-crystal methods

The molecular structure, showing thermal ellipsoids, obtained from the low-temperature determination of the metastable phase is shown in Fig. 1. The bond lengths, bond angles and torsion angles in the metastable phase are almost identical to those in the stable phase with two exceptions:

(i) The dihedral angle between the two phenyl rings is 64.5° in the metastable phase and 54.4° in the stable phase.

(ii) The central bond angle C8—C1—C2 at the carbonyl group is 118.9 (1)° in the metastable phase and 121.4 (2)° in the stable phase.

The metastable structure contains both enantiomers that arise as a consequence of the conformation of the benzo-

Table 7
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the metastable phase of benzophenone as found by single-crystal studies at 223 K.

Numbers associated with the H atoms indicate the C atom to which they are attached.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.37698 (8)	0.1592 (2)	0.97451 (8)	0.0539 (6)
C1	0.3758 (1)	0.2532 (2)	0.9152 (1)	0.0389 (8)
C2	0.4603 (1)	0.3130 (2)	0.9099 (1)	0.0374 (8)
C3	0.5373 (1)	0.2183 (2)	0.9444 (1)	0.0481 (10)
C4	0.6166 (1)	0.2743 (3)	0.9420 (1)	0.0574 (11)
C5	0.6207 (1)	0.4289 (3)	0.9073 (1)	0.0583 (12)
C6	0.5449 (1)	0.5242 (3)	0.8737 (1)	0.0562 (11)
C7	0.4648 (1)	0.4668 (2)	0.8739 (1)	0.0477 (10)
C8	0.2884 (1)	0.3088 (2)	0.8460 (1)	0.0380 (9)
C9	0.2187 (1)	0.3516 (2)	0.8713 (1)	0.0488 (10)
C10	0.1369 (1)	0.3984 (3)	0.8069 (2)	0.0595 (12)
C11	0.1238 (1)	0.3975 (2)	0.7180 (2)	0.0621 (12)
C12	0.1924 (1)	0.3539 (2)	0.6924 (1)	0.0571 (11)
C13	0.2750 (1)	0.3113 (2)	0.7566 (1)	0.0463 (9)
H3	0.533 (1)	0.108 (2)	0.967 (1)	0.057 (5)
H4	0.667 (1)	0.204 (3)	0.963 (1)	0.071 (6)
H5	0.680 (1)	0.467 (2)	0.908 (1)	0.063 (5)
H6	0.548 (1)	0.633 (2)	0.850 (1)	0.067 (5)
H7	0.412 (1)	0.535 (2)	0.850 (1)	0.057 (5)
H9	0.230 (1)	0.349 (2)	0.935 (1)	0.067 (6)
H10	0.092 (1)	0.429 (2)	0.827 (1)	0.066 (5)
H11	0.064 (1)	0.432 (3)	0.672 (1)	0.080 (6)
H12	0.185 (1)	0.354 (2)	0.630 (1)	0.070 (6)
H13	0.324 (1)	0.278 (2)	0.739 (1)	0.051 (5)

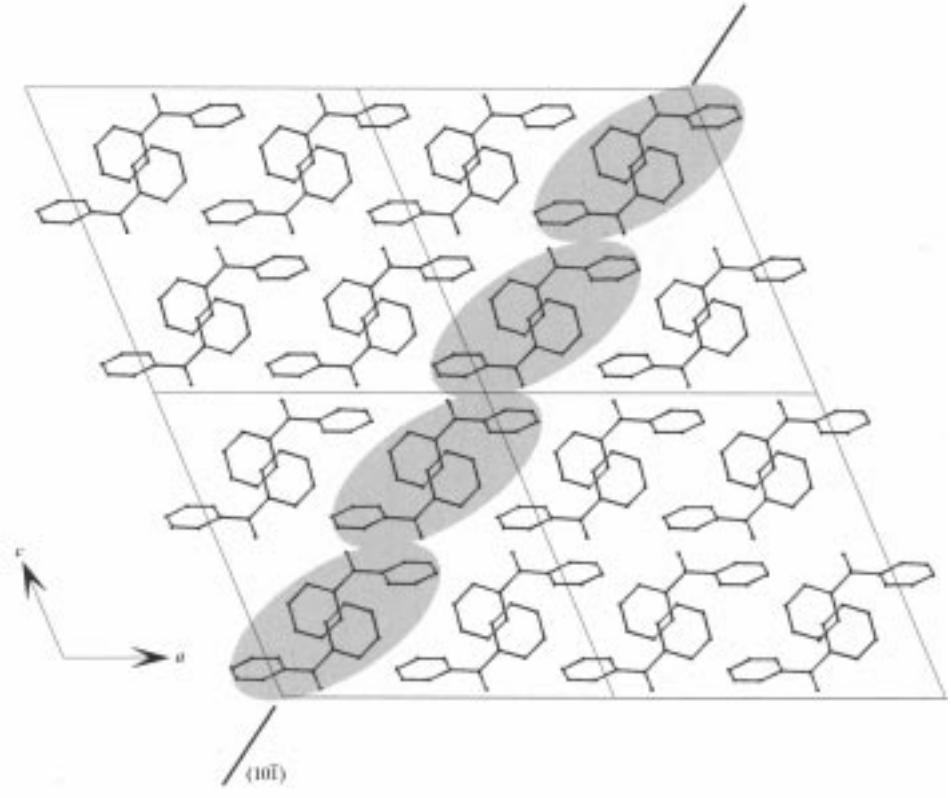


Figure 5
Molecular packing in metastable benzophenone viewed along the monoclinic **b** axis. The chains around the 2_1 axes, forming parallel (10$\bar{1}$) layers, are shadowed.

phenone molecule (the molecule cannot be superimposed on its mirror image), whereas the stable phase is built up from only one enantiomer and is thus capable of forming two enantiomorphs. The molecules of the metastable form are arranged in chains, containing the same enantiomer, aligned parallel to the monoclinic 2_1 axis. The handedness of adjacent chains in layers parallel to the (10$\bar{1}$) plane alternates as the chains are related by inversion centres, see Fig. 5. Neighbouring layers are symmetrically related by twofold axes, by inversion centres and by *c*-glide planes. The (10$\bar{1}$) layers correspond to the pinacoid {10$\bar{1}$}, which is one of the dominating face forms of the observed crystal morphology. Detailed intermolecular bond analyses show that this face is indeed an F-face (Hartman & Perdok, 1955*a*,*b*,*c*) containing two strong bond chains, one along the 2_1 axis and the other along the [101] direction.

Notwithstanding that the structures of the stable and metastable form of benzophenone are quite different, a certain similarity between them can be observed in projections along the monoclinic **b** axis of the metastable, and the orthorhombic **c** axis of the stable phase. Both directions are parallel to 2_1 screw axes and have nearly the same lattice translations: b = 8.104 and c = 7.996 Å, in the metastable and stable phases, respectively. In the stable phase, as in the metastable phase, chains aligned with the 2_1 axes exist, but in contrast to the metastable phase, they are all of one hand (Fig. 6). The elliptical cross-sections of adjacent chains are disposed to each other at an angle of ∼90°, leading to more ridged layers compared with the corresponding layers of the metastable phase (*cf.* Fig. 5). In the stable phase these layers occur in two equivalent orientations (110) and ($\bar{1}$01), which are F-faces and correspond to the predominant {110} prisms (*cf.* Fig. 3*a*) of the growth morphology (Roberts *et al.*, 1993).

5.3. Comparison with other benzophenone derivatives

Organic molecular compounds often crystallize in more than one modification. In many cases a metastable form can be obtained from a strongly supercooled melt. Amongst 'the old organic polymorphs', both the stable and metastable phases of a simple derivative of benzophenone, 4-methylbenzophenone, were recently studied by single-crystal analysis (Kutzke *et al.*, 1996). In the cases of both benzophenone and 4-methylbenzophenone, one form is

Table 8
Characteristic bond lengths (Å) and angles (°) of benzophenone from single-crystal structure determinations.

	Stable phase at 293 K (Girdwood, 1998)	Stable phase at 223 K (Kutzke, unpublished)	Metastable phase at 293 K (this work)	Metastable phase at 223 K (this work)
C1—O1	1.246	1.225 (3)	1.211 (7)	1.223 (2)
C1—C2	1.445	1.494 (3)	1.489 (8)	1.486 (2)
C1—C8	1.482	1.487 (3)	1.496 (9)	1.495 (2)
C2—C1—C8	123.48	121.4 (2)	117.1 (8)	118.9 (1)
C3—C2—C1—O1	26.4	28.1 (4)	27.0 (8)	27.2 (2)
O1—C1—C8—C9	29.1	26.9 (4)	41.2 (8)	41.9 (2)
Dihedral angle of the phenyl rings	54.4	54.4	64.3	64.5

enantiomorphous and the other racemic. Metastable 4-methylbenzophenone was first prepared in 1873 by Behr & van Dorp (1873) and has similar crystallization behaviour to benzophenone. Historically, this compound was the first metastable organic phase for which the crystal morphology, and some optical properties, were described in detail (Bodewig, 1876).

For benzophenone and its derivatives, the dihedral angle between the planes of the two phenyl rings is a critical parameter that may change considerably from that expected for an isolated molecule *in vacuo* to that actually observed in the solid-state phases (Roberts *et al.*, 1993). This change reflects the subtle influence of the crystal field on the molecular conformation and must occur during the process of crystal growth. In addition, it might be anticipated that the dihedral angle is likely to change from one polymorphic form to another, owing to the different packing configurations adopted. This expectation is confirmed by the dihedral angles observed for benzophenone and 4-methylbenzophenone listed in Table 9. These angles are within the range 46.3–68.7° (absolute values) found in the Cambridge Structural Database using the retrieval program *QUEST*3D (Allen & Kennard, 1993). The bond angles of the carbonyl group are quite similar in both modifications of 4-methylbenzophenone, but they differ by a few degrees in the two phases of benzophenone (Table 9). Their values are comparable with those of known derivatives of benzophenone, which range between 116.7 and 123.6°.

In addition to considering the molecular geometries of the stable and metastable modifications of benzophenone and 4-methylbenzophenone, a comparison of their densities and lattice energies is of special interest. Lattice energies were calculated using the program *HABIT* (Clydesdale *et al.*, 1991) and the force field after Momany *et al.* (1974). The values determined are given in Table 9. Given that these calculations yield potential energies at absolute zero, it is pleasing to note that the relative stability of the polymorphs of both materials, predicted by the calculations, is in agreement with that observed experimentally.

As well as having a more negative lattice energy, the stable polymorph of a material is expected to have a higher density. This condition is true for benzophenone, but not for 4-methylbenzophenone which has a slightly denser metastable modification. According to Wallach's Rule (Wallach, 1895), a racemic crystal should be denser, and hence more stable, than its chiral counterparts. Many exceptions to this rule exist and importantly benzophenone does not obey it. A detailed study of the density of chiral and racemic polymorphs and the validity of Wallach's rule is given by Brock *et al.* (1991).

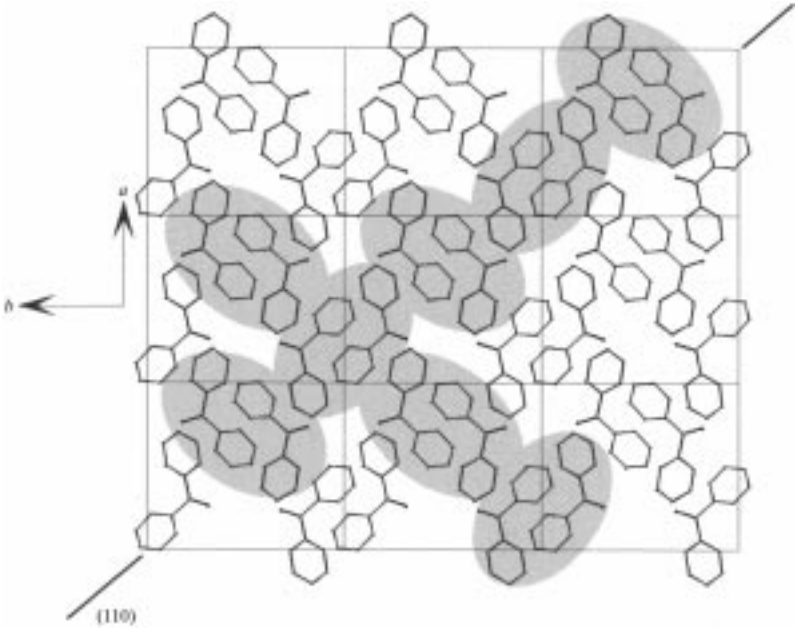


Figure 6
Molecular packing of stable benzophenone viewed along the orthorhombic **c** axis. The chains around the 2_1 axes, forming ridged layers parallel to (110) and ($1\bar{1}0$), are shadowed.

5.4. Monotropic transition into the stable phase

The two polymorphs of benzophenone consist of a left- or right-handed stable structure and a 'racemic' structure containing both enantiomers. During the monotropic transition into the stable phase, half the molecules switch configuration to form their mirror image. The transformation proceeds *via* two separate rotations with the same sense when viewed from the fixed position of the carbonyl carbon C1 looking along C1—C2 and C1—C8, respectively. The two phenyl rings rotate around, respectively, the C1—C2 and C1—C8 bonds into a configuration in which the inclina-

Table 9
Comparison of the two benzophenone polymorphs (at 223 K) with the two modifications of 4-methylbenzophenone (at room temperature), see Kutzke *et al.* (1996).

Compound	Space group	Melting point (K)	Density (g cm^{-3})	Lattice energy (kJ mol^{-1})	Dihedral angle (°)	Central bond angle C2—C1—C8 (°)
Stable benzophenone	$P2_12_12_1$	321	1.215	−85.90	54.4	121.4
Metastable benzophenone	$C2/c$	297–299	1.212	−83.01	64.5	118.9
Stable 4-methylbenzophenone	$P2_1/c$	331–332	1.173	−85.69	63.0	120.2
Metastable 4-methylbenzophenone	$P3_1$ resp. $P3_2$	327–328	1.179	−84.81	58.2	121.1

tions of the two rings (with respect to the C2—C1—C8 plane, *cf.* Fig. 1) are interchanged. Molecular mechanics calculations suggest that these mutual rotations proceed *via* the configuration in which the phenyl planes are normal to each other. This rotation path is subject to a relatively low energy barrier. The rotation *via* the parallel position of the phenyl planes is highly improbable owing to the large repulsive forces between the H atoms attached to the *ortho*-carbon atoms C7 and C13 (*cf.* Fig. 1). A detailed study of the energetics of conformational switching processes of a large number of benzophenone derivatives is given by Rappoport *et al.* (1990).

The phase transition is reconstructive and destroys any single crystal in which it occurs, leaving a polycrystalline aggregate of the stable phase that, nevertheless, retains the shape of the former single crystal. Visually the transition is manifested by the turbid appearance of the transformed regions. Once initiated at room temperature, the transition front proceeds through the crystal at a rate of a few millimetres per second.

6. Conclusions

The present paper reports structure determinations for metastable benzophenone which was first crystallized, and morphologically described as monoclinic, more than a hundred years ago. Hence, the century-old problem of the structural polymorphism of this well known organic compound has finally found its solution. It was observed that whereas the stable modification of benzophenone is enantiomorphous, the metastable form is racemic. Interestingly the same structural relationship, but opposite order of stability, is found for the polymorphs of 4-methylbenzophenone. Further investigations are required to show whether there is a more general rule for polymorphs crystallized from supercooled melts.

It is emphasized that the structure of metastable benzophenone was determined in two quite separate and simultaneous studies. In the first case, powder diffraction data were combined with a systematic computational search for trial structures in direct space, followed by Rietveld refinement of the best trial structure. In the second case, single-crystal X-ray diffraction analysis was employed. Both methods led, within the limits of their associated errors, to the same crystal structure. This overall study provides further evidence of the significant potential for solving the crystal structures of molecular materials using powder diffraction data, a crucial factor when suitable single crystals cannot be obtained.

Note added in proof: During the revision of this paper it became known that the structure of metastable benzophenone has been independently determined from single-crystal data by J. Bernstein and J.-O. Henck (Ben Gurion University of the Negev, Beer Sheva, Israel; private communication by J. Bernstein).

Our approach to structure solution from powder data has been developed *via* a long standing collaboration with Professor R. Docherty, (formerly of Zeneca Specialities, Blackley, Manchester, England, currently with Pfizer Central Research, Sandwich, Kent, England), whom we gratefully acknowledge. We thank the EPSRC for a grant (GR/L82373) to RBH and Dr L. Wiehl for helpful assistance in low-temperature single-crystal measurements.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Behr, A. & van Dorp, W. A. (1873). *Ber. Dtsch. Chem. Ges.* **6**, 754–755.
Bernstein, J. (1993). *J. Phys. D*, **26**, B66–B76.
Bleay, J., Hooper, R. M., Narang, R. S. & Sherwood, J. N. (1978). *J. Cryst. Growth*, **43**, 589–596.
Bodewig, C. (1876). *Ann. Phys.* **158**, 235–239.
Borisov, A. G. (1993). *Kristallografiya*, **38**, 217–237.
Boultif, F. & Louer, D. (1991). *J. Appl. Cryst.* **24**, 987–993.
Brock, C. P., Schweizer, W. P. & Dunitz, J. D. (1991). *J. Am. Chem. Soc.* **113**, 9811–9820.
Buerger, M. J. & Bloom, M. C (1937). *Z. Kristallogr.* **96**, 182–190.
Clydesdale, G., Docherty, R. & Roberts, K. J. (1991). *Comput. Phys. Commun.* **64**, 315–331.
Dunitz, J. D. & Bernstein, J. (1995). *Acc. Chem. Res.* **28**, 193–200.
Fleischer, E. B., Sung, N. & Hawkinson, S. (1968). *J. Phys. Chem.* **72**, 4311–4312.
Girdwood, S. (1998). Ph.D. Thesis. Strathclyde University, Glasgow, Scotland.
Gossner, B. (1904). *Z. Kristallogr.* **38**, 110–122.
Graham, D. J., Magdolinos, P. & Tosi, M. (1995). *J. Phys. Chem.* **99**, 4757–4762.
Groth, P. (1919). *Chemische Krystallographie, Band V*, p. 89. Leipzig: W. Engelmann.
Hammond, R. B., Roberts, K. J., Docherty, R. & Edmondson, M. (1997). *J. Phys. Chem. B*, **101**, 6532–6536.

Hartman, P. & Perdok, W. G. (1955*a*). *Acta Cryst.* **8**, 49–52.
Hartman, P. & Perdok, W. G. (1955*b*). *Acta Cryst.* **8**, 521–524.
Hartman, P. & Perdok, W. G. (1955*c*). *Acta Cryst.* **8**, 525–529.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kutzke, H., Al-Mansour, M. & Klapper, H. (1996). *J. Mol. Struct.* **374**, 129–135.
Larson, A. C. & Von Dreele, R. B. (1985). *GSAS*. LANCE, MS-H805. Los Alamos National Laboratory, Los Alamos, NM 87545, USA.
Laurent, M. A. (1842). *Compt. Rend.* **15**, 350–353.
Le Bail, A., Duroy, H. & Fourquet, J. L. (1988). *Mater. Res. Bull.* **23**, 447–452.
Lehmann, O. (1877). *Z. Kristallogr.* **1**, 97–131.
Linnemann, E. (1865). *Ann. D. Chem.* **133**, 1–4.
Lobanova, G. M. (1968). *Kristallografiya*, **13**, 984–986.
Mayo, S. L., Olafson, B. D. & Goddard III, W. A. (1990). *J. Phys. Chem.* **94,** 8897–8909.
Melnik, V. I., Nelipovich, K. I. & Shpak, M. T. (1980). *Ivz. Akad. Nauk. SSSR Ser. Fiz.* **44**, 827–832.
Molecular Simulations Inc. (1998). *Cerius*^{2} *Molecular Simulation Software*. Molecular Simulations Inc., San Diego, USA (http://www.msi.com.).
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*, Version 5.0. MSC, The Woodlands, TX 77381, USA.
Momany, F. A., Carruthers, L. M., McGuire, R. F. & Scheraga, H. A. (1974). *J. Phys. Chem.* **78**, 1595–1620.
Nacken, R. (1915). *Neues Jahrb. Mineral. Geol. Palaeontol.* 133–164.
Prendel, R. (1892). *Z. Kristallogr.* **24**, 516.
Rappoport, Z., Biali, S. E. & Kaftory, M. (1990). *J. Am. Chem. Soc.* **112**, 7742–7748.
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
Roberts, K. J., Docherty, R., Bennema, P. & Jetten, L. A. M. J. (1993). *J. Phys. D*, **26**, B7–B21.
Schaum, K. (1897). *Die Arten der Isomerie.* Marburg: Habilitation.
Schaum, K. (1914). *Chem. Ztg*, **23**, 257–258.
Schaum, K. & Schoenbeck, F. (1902). *Ann. Phys.* **4**, 652–662.
Stewart, J. P. (1990). *J. Comput.-Aided Mol. Des.* **4**, 1–105.
Tanatar, S. (1892). *Russ. Fiz.-Chim. Ob. J.* **1**, 621–624.
Visser, W. (1969). *J. Appl. Cryst.* **2**, 89–95.
Vul, E. B. & Lobanova, G. M. (1967). *Kristallografiya*, **12**, 411–415.
Wallach, O. (1895). *Liebigs Ann. Chem.* **286**, 90–143.
Wickel, E. (1886). *Z. Kristallogr.* **11**, 78–83.
Woehler, F. & Liebig, J. (1832). *Ann. Chem.* **3**, 249–287.
Zincke, T. (1871). *Ann. Chem.* **159**, 378–383.