Investigation of the structural phase transitions near 190 K in 4,4′-dichlorobenzophenone

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Abstract

X-ray structure studies have been carried out on single crystals of 4,4′-dichlorobenzophenone at temperatures from 164 to 295 K. The structure determined at 164 K is monoclinic $I2/c$. Crystal data: $T = 164$ K; $a = 24.527$ (6), $b = 6.064$ (1), $c = 7.457$ (4) Å; $\beta = 100.10$ (2)°; $V = 1091.9$ (6) Å^3; $Z = 4$; $d_c = 1.528$ g cm^{-3}; λ(Mo $K\alpha$) $= 0.71073$ Å; $\mu = 0.565$ mm^{-1}; $F(000) = 512$; $R = 0.04$. The temperature dependence of the unit-cell parameters and of the intensities of some symmetry-sensitive reflections has been measured over the range 164–293 K, both in warm-up and cool-down experiments. It has been established that the phase transformation between the $C2/c$ and $I2/c$ structures occurs as a sequence of two closely spaced first-order phase transitions. In between these phase transitions the crystal is in an intermediate state whose structure is different from both $C2/c$ and $I2/c$. The experimental data give us ground to suppose that the intermediate state is disordered, having a primitive cell half as large as in the two ordered phases. Within the temperature interval where the said intermediate state exists the thermal expansivity along axis c is negative.

1. Introduction

Crystals consisting of flexible carbonyl molecules make up a rather large group of solids, in which temperature and pressure are able to produce changes in the fine balance of intra- and intermolecular interactions (Chan, 1987; Nakayama *et al.*, 1994, 1995; Kirin & Pawley, 1982, 1987; Peretti & Ranson, 1979). The 4,4′-dichloro-benzophenone (DCBP) crystal attracts special attention, because an intriguing sequence of phase transitions has been reported for this compound around 190 K at ambient pressure. Presumably the same transition can be driven at room temperature by pressure (Kirin & Pawley, 1982). These transitions have been extensively studied by NMR, NQR, Raman, thermal *etc.* techniques (see *e.g.* Nakayama *et al.*, 1994; Nakayama *et al.*, 1995; Peretti & Ranson, 1979; Wolfenson *et al.*, 1990, and the literature quoted therein). The room-temperature structure of 4,4′-dichlorobenzophenone was determined previously (Shields & Kennard, 1977; Granger &

Coillot, 1985) to be $C2/c$.† Recently, Zúñiga & Criado (1995) determined the structure of DCBP at 140 K and showed that the space-group symmetry at that temperature was $I2/c$. These authors suggested that the DCBP crystal between 190 and 140 K was in an intermediate phase modulated along the x axis. Their findings corroborate the inference drawn from Raman scattering data (Kirin & Pawley, 1987; Peretti & Ranson, 1979; Wolfenson *et al.*, 1990) that symmetry remains unchanged across the transition. Although Zúñiga & Criado (1995) state that they saw indications of an intermediate (between C and I) phase between 190 and 140 K, they did not report any relevant quantitative structure data.

The results and conclusions of different groups differ greatly regarding such crucial questions as the number of phase transitions, their nature and the temperature range where the phase transformation occurs. Raman spectroscopy data (Peretti & Ranson, 1979) indicate that some phase transformations take place between 165 and 190 K. On the other hand, NQR and thermal measurements give evidence (Nakayama *et al.*, 1994; Wolfenson *et al.*, 1990) that within a certain interval close to 190 K several phase transitions occur, invoking the existence of an intermediate, possibly incommensurate, phase.

The nature of the transition (or transitions) itself, as well as of the intermediate states involved, needed a more accurate structural investigation, which constitutes the aim of the present paper. We should add here that actually all the results in this paper were obtained before we came across the paper by Zúñiga & Criado (1995) on the low-temperature structure of 4,4′-dichloro-benzophenone, which could not be ignored during the preparation of our manuscript.

2. Experimental

It is commonly accepted that lattice imperfections of a solid undergoing a first-order displacement-type transition are a major factor controlling the kinetics of this phase transition. In our opinion, the above-mentioned existing contradictions between the conclusions of

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† There is also a publication (Toussaint, 1948) in which the room-temperature structure was reconstructed only partially.

different workers are, at least in part, related to the different purities of the samples. This is why we paid special attention to the purity of the crystals to be studied. The commercial compound 4,4′-dichloro-benzophenone was purified by chromatography and multiple (100 passes) zone melting. The final very high purity of the material after purification can be inferred from the long exciton lifetimes (15 μs and longer), as observed at liquid-helium temperature by phosphorescence (Avdeenko *et al.*, 1980).

Single crystals of 4,4′-dichlorobenzophenone for X-ray studies were grown by sublimational re-deposition in an evacuated glass ampoule. For experiments we chose a few plate-shaped single crystals with dimensions approximately 0.3 × 0.5 × 0.5 mm³. Experiments were performed on an automated SYNTEX P2₁ diffractometer with a low-temperature LT-1 device using Mo *K*α radiation (graphite monochromator). The temperature was controlled by means of a copper-constantan thermocouple, reliably secured at the centerline of the coolant flow at a distance of 3–4 mm from the sample. The accuracy was at least 1 K during data collection and better than 0.3 K during lattice parameter measurements, owing to electronic flow temperature stabilization. The improved flow stability made it possible to reliably detect a temperature interval with negative expansion coefficient along the *c* axis, which otherwise looked like a set of data points with an abnormally broad scatter.

The lattice parameters were determined within the temperature range 160–295 K by least-squares analysis using the same set of 15 *hkl* reflections with 2θ close to 30°. It is noteworthy that the orientation matrix suffered only minor variations owing to thermal contraction and phase transition discontinuity. To eliminate the errors associated with the thermal deformations of the sample holder, we made visual adjustment of the sample every 10–15 K. This factor could be the source of the scatter of the measured lattice parameters.

Simultaneously with lattice parameter measurements we determined integrated intensities as a function of temperature for three pairs of sufficiently strong special reflections. We took one pair of reflections that are strong within the range where the *C* phase exists (11$\bar{1}$ and 111 with *I* > 10⁵ at room temperature), a pair of *I*-type reflections (011 and 031 with *I* > 10⁵ at 164 K) and a pair of symmetry-indifferent reflections (022 and 222 with *I* > 10⁵ over the entire temperature range studied).

At 140 K the 4,4′-dichlorobenzophenone crystal is monoclinic, space group *I2/c* (Zúñiga & Criado, 1995). It follows from our data on the temperature dependence of both the lattice parameters and the intensities of the above reflections that the LT phase *I2/c* forms, as we go down in temperature, much earlier than inferred by Zúñiga & Criado (1995). To test this conclusion, we collected data at 164 K. We have determined the structure of DCBP at 164 K to be monoclinic, space group

I2/c, without any significant violation of *I2/c* symmetry. The crystal data and the data collection parameters are summarized in Table 1.†

The structure at 164 K was refined, assuming, as was performed by Zúñiga & Criado (1995), that the asymmetric unit of the 4,4′-dichlorobenzophenone molecule occupies the same special position as in the high-temperature *C2/c* phase, yet the multiplication rules are different, corresponding to space group *I2/c*. The starting value of the *R* factor in isotropic approximation for non-H atoms was approximately 40%; a few structure refinement cycles within the isotropic approximation reduced *R* to 0.11. The structure was finally refined to F_o^2 in an approximation, isotropic for H atoms and anisotropic for the other atoms. The overall number of refined parameters was 91, including the isotropic extinction. The final residual *R* values are *R* = 0.040 for 842 reflections with $F_o > 4\sigma(F_o)$ and *R* = 0.052 for all 945 reflections.

Computations were performed using program packages *XTL* for preliminary structure determination and *SHELXTL/PC* (Sheldrick, 1993) for final refinement.

3. Results and discussion

As the first step we determined the room-temperature structure of 4,4′-dibenzophenone (*R* = 0.046 over all observed reflections), which turned out to be in good agreement with results available (Shields & Kennard, 1977; Granger & Coillot, 1985) regarding both the molecular geometry and the lattice parameters.

At 164 K, the diffraction pattern contains clearly observable general-type reflections with odd *h* + *k* values, which are systematically absent in the high-temperature *C* symmetry. For the reflections collected at 164 K we found the following systematic absence rules: general *hkl* with *h* + *k* + *l* = 2*n* + 1; *h*0*l* with *h* = 2*n* + 1 and *l* = 2*n* + 1, which corresponds to space group *I2/c*. ‡ The positional and thermal parameters of the atoms in the DCBP crystal obtained in our studies at 164 K are in good agreement with the relevant data at 140 K of Zúñiga & Criado (1995). This also applies to molecular geometry.

The structural phase transformation near 190 K in DCBP consists of the following (see Fig. 1). Both in the high-temperature (HT) and low-temperature (LT) structures the molecules are arranged along the *c* axis in rows (vertical rows in Fig. 1) with the C7—O bond vector being directed alternately up and down within

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: HR0042). Services for accessing these data are described at the back of the journal.

‡ The elementary cell parameters of DCBP at 164 K in the *C2/c* setting (with an orientation matrix which is basically different from that used during data collection) are *a* = 24.352 (6), *b* = 6.064 (1), *c* = 7.457 (4) Å; β = 97.45 (2)° (*cf.* those above in the *I2/c* setting).

Table 1. *Experimental details*

Crystal data

Chemical formula	$C_{13}H_8Cl_2O$
Chemical formula weight	251.09
Cell setting	Monoclinic
Space group	$I2/c$
a (Å)	24.527 (6)
b (Å)	6.0640 (10)
c (Å)	7.457 (4)
β (°)	100.10 (2)
V (Å^3)	1091.9 (7)
Z	4
D_x (Mg m^{-3})	1.52
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	15
θ range (°)	15–16
μ (mm^{-1})	0.565
Temperature (K)	164 (2)
Crystal form	Plate
Crystal size (mm)	$0.50 \times 0.50 \times 0.30$
Crystal color	Transparent

Data collection

Diffractometer	SYNTEX P2$_1$
Data collection method	ω–2θ scans
Absorption correction	None
No. of measured reflections	1025
No. of independent reflections	945
No. of observed reflections	842
Criterion for observed reflections	$F > 4\sigma(F)$
R_{int}	0.1155
θ_{max} (°)	25.05
Range of h, k, l	$0 \rightarrow h \rightarrow 29$
	$-1 \rightarrow k \rightarrow 7$
	$-8 \rightarrow l \rightarrow 8$
No. of standard reflections	3
Frequency of standard reflections	Every 97 reflections
Intensity decay (%)	None

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0399
$wR(^2)$	0.1449
S	1.194
No. of reflections used in refinement	898
No. of parameters used	91
H-atom treatment	Isotropic
Weighting scheme	$w = 1/[\sigma^2(F_o^2 + (0.0457P)^2 + 2.5539P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	< 0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.326
$\Delta\rho_{min}$ (e Å^{-3})	−0.320
Extinction method	SHELXL93 (Sheldrick, 1993)
Extinction coefficient	0.0040 (13)
Source of atomic scattering factors	International Tables for Crystallography (Vol. C)

Computer programs

Data collection	Recentering 2T/T (Operations Manual SYNTEX P2$_1$; Cupertino, 1973)
Cell refinement	Least-Squares Orientation Matrix Program (Cupertino, 1973)
Structure solution	SHELXS86 (Sheldrick, 1990)
Structure refinement	SHELXL93 (Sheldrick, 1993)

every row. Moreover, the structure of *bc* molecular layers in both phases is the same, since they are formed by equivalent symmetry elements from asymmetric units with virtually the same positional parameters. It should be noted that the molecular conformation is basically the same in both phases, which is typical of structural phase transitions in molecular crystals (Botoshansky *et al.*, 1998). In both phases two *bc* layers, which form vertical rows in Fig. 1, comprise the unit cell. The difference between the HT and LT phases is in a different mutual arrangement to those layers. In the HT phase two neighboring layers are related by the $[\frac{1}{2},\frac{1}{2},0]$ translation, which corresponds to C symmetry, whereas in the LT phase this translation is $[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ corresponding to I symmetry. Such a transformation can occur, for example, as a **c**/2 shift of every second *bc* layer, which in Fig. 1 looks like a **c**/2 shift of the base-centering row. We also note here that every row along **c** contains alternating enantiomers of DCBP molecules. This is why the phase transition mechanism must be of a displacement nature, because any rotations of the molecule as a whole are unable to transform one enantiomer into another.
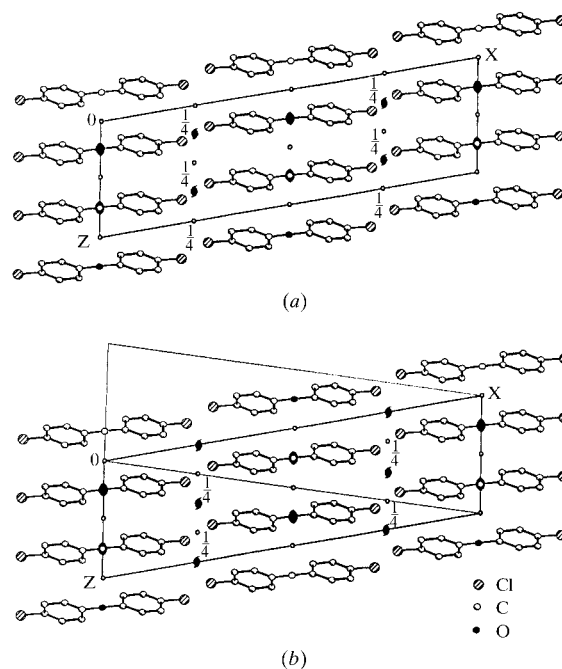

Fig. 1. Projection on the *ac* plane of the 4,4′-dichlorobenzophenone crystal structure (*a*) at room temperature and (*b*) at 164 K. To indicate the direction of the C7—O bond, two variants of the twofold axis symbol are utilized. The standard symbol is used when the C7—O bond is upwards out of the plane of the figure. The twofold axis symbol with a white central spot is used for indicating the enantiomeric molecule with the C7—O bond pointing in the opposite direction. The low-temperature structure can be obtained from the upper drawing by shifting the middle vertical row of molecules by **c**/2. A standard set of new *C2/c* elementary cells for the LT phase rather than the chosen *I2/c* set is marked by thin lines (see second footnote on p. 800).

We found that at room temperature the angle between phenyl rings is 50.6°, which compares well with the earlier results: 50.7° by Shields & Kennard (1977) and 50.2° by Granger & Coillot (1985); our own recalculation from their atomic positions yields 50.54°. The angle between phenyl rings, which is an important conformational parameter of the DCBP molecule, varies from 50.6° at 295 K to 49.7° at 164 K. It should be noted that the relative variation of this angle amounted to 1.8%, which is comparable with the overall relative change of the unit-cell parameters. Thus, the conformational response of the DCBP molecule in the crystal is of the same magnitude as the variation of the other lattice characteristics.
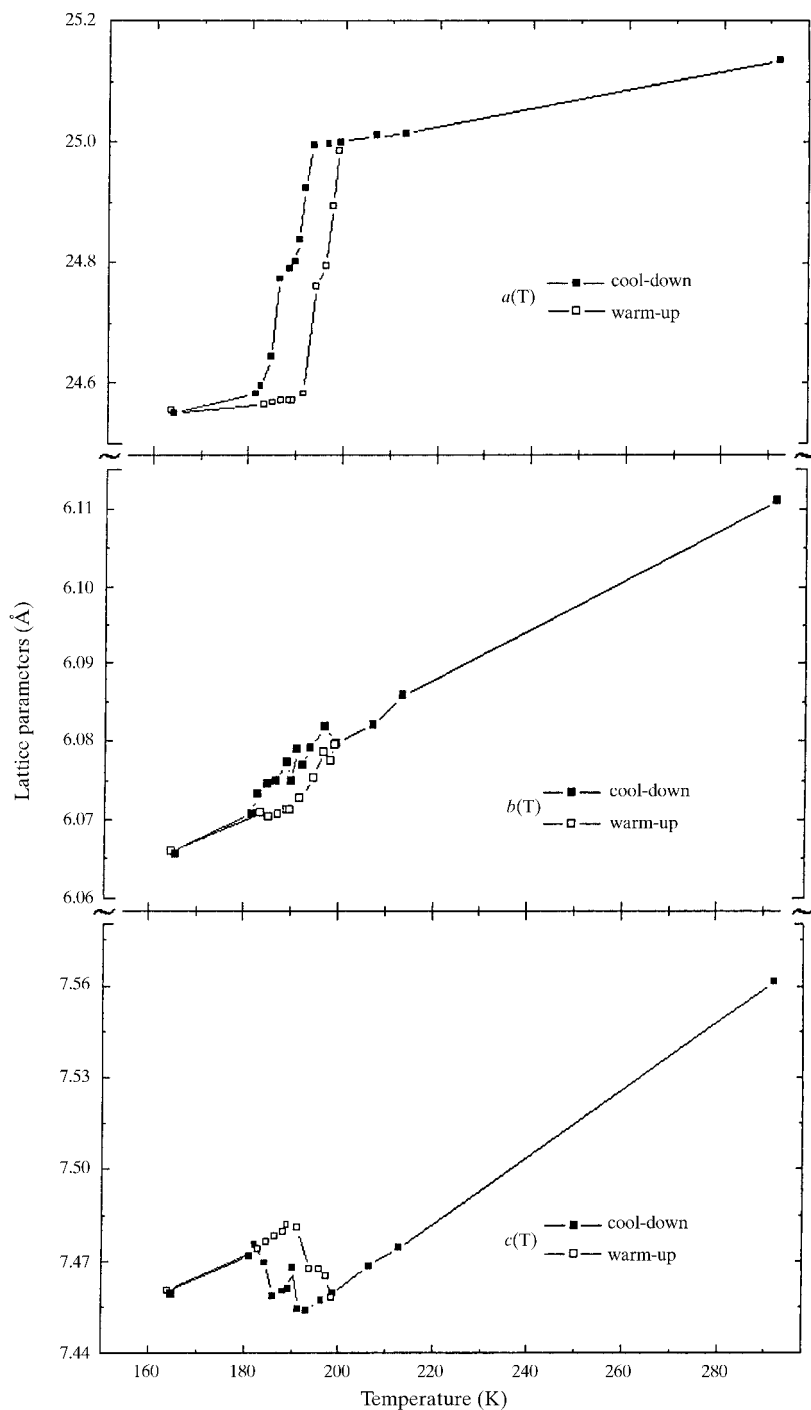

Fig. 2. Temperature dependence of the unit-cell parameters (top to bottom) $a(T)$, $b(T)$ and $c(T)$. Solid and empty symbols show cool-down and warm-up data, respectively.

We measured variations of the DCBP unit-cell parameters over the range 164–295 K, both with warm-up and cool-down. The corresponding plots for the lattice parameters *a*, *b* and *c* are shown in Fig. 2; the monoclinic angle and the unit-cell volume *versus* temperature are given in Fig. 3; warm-up data are shown everywhere as empty symbols and cool-down data as solid ones. All the parameters exhibit clearly visible hysteresis, the typical hysteretic span in temperature being ∼10 K, irrespective of the parameter. The lattice parameters α and β are obviously discontinuous at 189 K, in agreement with the earlier conclusions (Nakayama *et al.*, 1994) that the transition under consideration is of first order. The *b versus* temperature curves run without manifestly abrupt changes. The temperature variation of the lattice parameter $c(T)$ did show a discontinuity, but of negative sign. There is an unusual feature, *viz.* a clearly stepwise variation of any of the lattice parameters within the interval where the phase transition takes place (see Figs. 2 and 3). The volume jump, which is almost completely due to the change of the lattice parameter *a* across the transition, is ∼1.8%.

To understand if the transition under consideration and the pressure-driven transition (Kirin & Pawley, 1982) are the same, let us now compare our findings with what can be inferred from the value of the pressure needed to drive the transition. At pressures between 3 and 5 kbar the low-lying Raman frequencies exhibit variations that can be interpreted as indications of a phase transition. (We remark here that this Raman experiment was carried out on a powder sample, which might be the source of the rather large pressure span.) We proceed from the consideration that the thermal contraction of a sufficient magnitude must result in the same phase transition as that driven by pressure at a comparable compression. The relative volume change $\Delta V/V$ brought about by the pressure *P* can be evaluated as follows

$$\Delta V/V = P \sum_i A_i \tag{1}$$

with

$$A_1 = s_{11} + s_{21} + s_{31}$$
$$A_2 = s_{12} + s_{22} + s_{32}$$
$$A_3 = s_{13} + s_{23} + s_{33}, \tag{2}$$

where s_{ij} is the compliance tensor of the material. The elastic constants are not available for DCBP. However, considering the fact that many different substances such as naphthalene, dibenzyl and stilbene have similar room-temperature compliance tensor values (Kitaigorodski, 1973), we took s_{ij} values for dibenzyl. We estimate the compression to be (6.4–10.7)%, which compares well with our overall volume decrease of 4.6% from room temperature to the transition point. This allows us to assert that the transition under study and the pressure-driven transformation have a common formal cause, namely the diminishing of the cell dimensions.

Important information can be obtained from the temperature dependence of the intensities of the three types of reflections mentioned above, one type with indices characteristic of the *C* symmetry (these reflections are strictly zero in the *I* phase), another type with indices characteristic of the *I* symmetry (absent in the *C* phase) and still another type, which is present both in the *I* and *C* phases. We recorded intensities of two reflections for each type, or six all in all. Fig. 4 shows the intensities of one *C*-type (111) and one *I*-type (031) reflections for warm-up and cool-down runs. The measured intensities are presented normalized to the intensity values at the respective temperatures, $I_{hkl}(T)/I_{hkl}(293)$ for *C*-type and $I_{hkl}(T)/I_{hkl}(164)$ for *I*-type reflections. (To avoid overcrowding we do not plot other curves; the intensity of the 'symmetry-
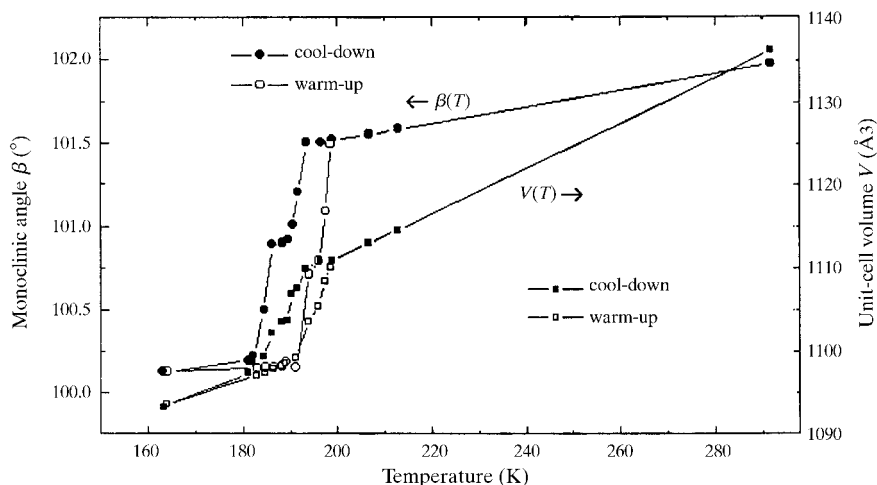

Fig. 3. Temperature dependence of the monoclinic angle $\beta(T)$ (left axis) and the elementary cell volume $V(T)$ (right axis). Solid and empty symbols show cool-down and warm-up data, respectively.

indifferent' reflections behave smoothly, showing only a minor decrease within the 10 K range where the transition occurs.) As with the lattice parameters, the intensities exhibit hysteresis. One can notice that the temperature interval where the low-temperature phase forms is much broader than the intervals within which both phases disappear.

The reduced intensity of the corresponding reflection can be treated as the fraction of the sample volume which is in one of the two possible phases, C or I in our case. For example, at room temperature the whole volume is in the C phase and the volume of the I phase is zero (at 164 K, on the contrary). As one can see from Fig. 4, there exists a temperature interval, $\sim$10 K wide during cool-down, where the sum $I_{111} + I_{031}$ is much less than unity. This means that the state of the sample cannot be described only by two phases. In other words, within this temperature interval the structure of the crystal is different from the HT phase $C2/c$, existing above the transition point, as well as from the LT phase $I2/c$, which according to our data exists at temperatures as high as 164 K and not below 140 K, as seen from the data of Zúñiga & Criado (1995). The intensities of another pair of reflections, $11\bar{1}$ and 011, behave exactly in the same way. The inference of an intermediate state, which cannot be described by a superposition of the C and I lattices, is also corroborated by the following. The ratio $I_{11\bar{1}}/I_{111}$ does not vary appreciably from room temperature down to the transition point. Within the said temperature interval this ratio changes considerably from the value characteristic of the C phase. The same is true for the quantity I_{011}/I_{031} with respect to the value characteristic of the I phase at 164 K. All the above facts constitute evidence that the structure of DCBP in the intermediate state roughly between 180 and 195 K is, strictly speaking, neither C nor I.

Let us inspect temperature dependence of the reduced intensities (Fig. 4) in more detail. To be specific, let us consider the cool-down run for the C-type reflection 111. Down to the point $T \simeq 193.5$ K the reduced intensity is very close to unity, i.e. the entire volume is occupied by the C phase, which to within the thermal contraction coincides with the high-temperature structure. Below that point, the intensity of the reflection under consideration drops sharply (within a narrow interval of $\sim$1 K), but no corresponding increase of the I-line intensities is observed, as one might have expected in the standard 'two-phase' scenario of any first-order phase transition. Within $\sim$192 and 186 K the intensities of both C and I lines, although observable, are weaker by at least two orders of magnitude than in the respective mono-phase states. Even further below this range (from 186 down to 180 K) the I-type intensities build up steeply, whereas the C-type reflections die out completely. At still lower temperatures, down to 164 K, we observe the one-phase state of symmetry I, without any 'admixture' of the C phase.

The sample exhibits analogous behavior in the opposite sense during warm-up. The interval where the intermediate state exists during warm-up is at least half as wide as that observed for cool-down.

As one can see from Fig. 4, the intensity of any 'symmetry-sensitive' reflection (those shown in the plot as well as the absent ones, $11\bar{1}$ and 011) demonstrates a standard hysteresis loop with backstroke overlap. The hysteresis loop of the I-line 031 is noticeably broader than that of the C-line $11\bar{1}$.† As generally accepted, the temperature of the loop center can be treated as the corresponding first-order phase transition point.

Thus, we can state that the structural phase transformation between the $C2/c$ and $I2/c$ phases occurs as a sequence of two first-order transitions. The upper one, positioned at $T_c^{(up)} \simeq 195$ K from the hysteresis loop shape of the intensity of 111, is associated with the disappearance of the HT phase C and the formation of an intermediate state. The lower transition at $T_c^{(low)} \simeq 188$ K, as inferred from the 031 line intensity hysteresis, is from the above-mentioned intermediate state to the LT phase $I2/c$. The overall behavior is much in line with the NQR results of Wolfenson et al. (1990) and at variance with the structure findings of Zúñiga & Criado (1995), who saw an intermediate state down to 140 K.

Now, what can we say about the nature of the intermediate state. As can be seen from Fig. 4 for the cool-down data, below 193 K a new absence rule comes into force for reflections with odd $h + k + l$, which corresponds to the appearance of the I symmetry, although down to 185 K the reflections 111 and $11\bar{1}$ are still observable [their intensities I exceed $3\sigma(I)$], but by two orders of magnitude weaker than at 200 K. On the other hand, within this very temperature interval the general-type reflections with odd $h + k$, although just observable [$I > 3\sigma(I)$], are two orders of magnitude weaker than at 164 K. A similar behavior was observed during warm-up runs. In other words, we can state that in the intermediate state both 'quasi-absence' rules hold. This means that the crystal has a primitive cell with twofold shrinking of the initial parameter c rather than to a doubling along a as inferred by Zúñiga & Criado (1995). It is obvious that the halving of the elementary cell means that the intermediate state is disordered.

Formation of the disordered intermediate state can proceed as follows. For instance, if at the upper transition the fraction of the bc layers that underwent the shift by $\mathbf{c}/2$ is not one half, as needed for the complete transformation from $C2/c$ to $I2/c$ (see above), but close to 1/4, then the disordering would be complete. We point out that the intermediate state must be a mixture of the quasi-C and quasi-I lattices in order that both absences be almost rigorously observed experimentally.

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† One can see in Fig. 2(c) that the hysteresis of the lattice parameter c is broader near the lower transition point.

The same result can be obtained by introducing stacking faults (shifts of adjacent C areas by $\mathbf{c}/2$) into the initial C phase. Both these mechanisms, if brought to one half of what is needed to complete the transformation from C to I, would result in a monoclinic primitive cell with the asymmetric unit consisting of two DCBP enantiomers with opposite orientations of the C=O bond with almost equal probabilities of 0.5. Such a cell comprises four different Cl atoms, which might be responsible for the four presumably NQR frequencies observed in the intermediate state (Wolfenson *et al.*, 1990). In our view, the existence of the coherent boundary between the C and I phases results in numerous ways in which the final result will be the same from the viewpoint of diffraction.

The existence of intermediate phases, in which the disordering agents are presumably stacking faults, is quite common for displacement-type phase transitions such as , for example, the Pa3–hcp transition in *ortho*-H_2 or *para*-D_2 (Schuch *et al.*, 1968).

An extra argument for disordering is as follows. The c axis is the direction of the so-called stacking van der Waals contact. The net thermal expansion within the temperature interval studied is the largest, which is typical of solids made up of aromatic molecules. Therefore, the fact that within the interval where the intermediate phase exists the thermal expansivity along the c axis is negative is a manifestation of disorder (or even disappearance of strict periodicity, *i.e.* melting in this 'subsystem'). The persistence of the single crystallinity is not very surprising in view of, first, the unique closeness of the lattice parameters of both I and C phases and, second, the existence of coherent boundary between the two phases.

We believe that to a large extent the discrepancies between our results and the conclusions of various workers about the nature of the intermediate phase can be attributed to the differences in purity of the samples studied. The latest results of Zúñiga & Criado (1995)

have been obtained on DCBP crystals grown by evaporation from benzene solutions. This is likely to be the reason why the lattice parameters of the DCBP samples studied by Zúñiga & Criado (1995) at 140 K are larger than ours at 164 K (24 K higher).

Coming back to the temperature dependence of the unit-cell parameters (Figs. 2 and 3), it is clear that the relevant curves contain manifestations of the two phase transitions. First, the hysteresis widths in the upper and lower parts differ noticeably. Second, the unit-cell parameters vary obviously in a step-wise manner [which is especially clearly seen in the curves $a(T)$ and $\beta(T)$]. The steps are at the middle of the intervals where the respective parameter varies. It should be stressed that the lattice that corresponds to the intermediate state has parameters approximately between those in the C and I phases. This argument renders more convincing the model of the intermediate state as a 50/50 mixture of the quasi-I and quasi-C lattices, which is naturally disordered. The anomalies listed are completely in line with the conclusions based on the temperature behavior of the intensities of symmetry-sensitive reflections.

Summing up, we draw the following conclusions:

(i) From the temperature dependence of the lattice parameters and the intensity of some symmetry-sensitive reflections we conclude that the phase transformation in 4,4′-didichlorobenzophenone occurs as a sequence of two separate first-order transitions, with an intermediate state between the low-temperature $I2/c$ and high-temperature $C2/c$ phases, in accordance with the findings of Zúñiga & Criado (1995). This transition is characterized by a relatively narrow hysteresis and a volume jump (of ∼1%, mainly due to the variation of the longest cell dimension a).

(ii) Analysis of our lattice parameter data and the Raman scattering findings of Kirin & Pawley (1982) under moderate pressure provides grounds to assume that this phase transition is driven when the molecules are brought closer either by thermal contraction or
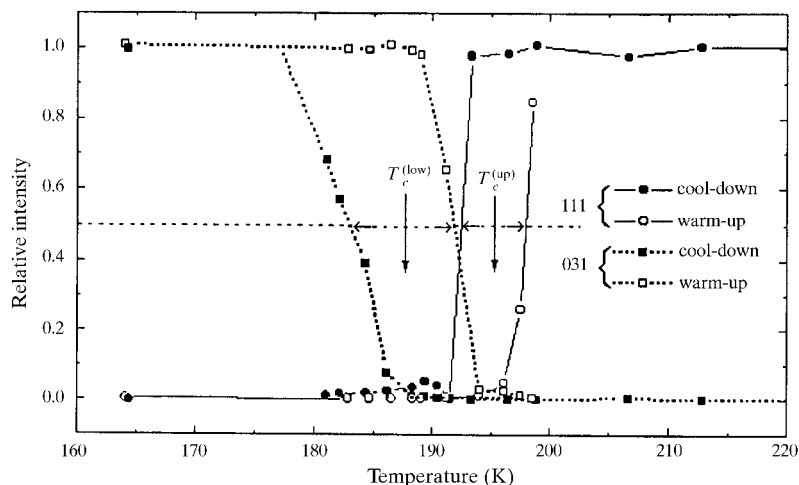

Fig. 4. Temperature dependence of the intensities of the reflections indicated. Solid and empty symbols show cool-down and warm-up data, respectively.

external pressure. The temperature points for both warm-up and cool-down runs in our experiments are in good agreement with the NQR data of Wolfenson *et al.* (1990) and do not agree with X-ray findings of Zúñiga & Criado (1995).

(iii) The intermediate state is found to have an effectively monoclinic primitive elementary cell of volume $\frac{1}{2}$ of the basic one. We believe that this new phase is a partially disordered state intermediate between C and I with a primitive unit cell half the size of the centred cells rather than a modulated structure with an almost doubled (along the a axis) cell, as found by Zúñiga & Criado (1995).

(iv) It is very likely that the phenomena observed in the structural phase transformation in 4,4′-didichlorobenzophenone are common to many first-order displacement-type transitions in solids between well defined ordered states.

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