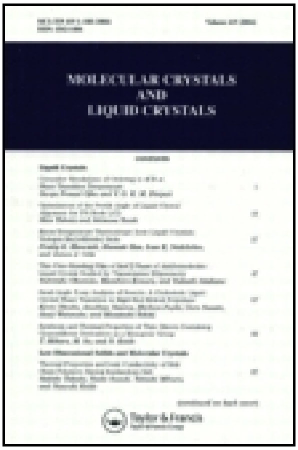

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Evidence for a Phase Transition in Crystalline 2-3 Dimethyl 1-4 Naphthoquinone

M. Breton [a] , N. B. Chanh [a] , J. Housty [a] & D. Louer [b]
[a] Laboratoire de Cristallographie et Physique Cristalline. Université de Bordeaux I, (France)
[b] Laboratoire de Cristallochimie. Universite de Rennes, (France)

Version of record first published: 28 Mar 2007.

To cite this article: M. Breton , N. B. Chanh , J. Housty & D. Louer (1976): Evidence for a Phase Transition in Crystalline 2-3 Dimethyl 1-4 Naphthoquinone, Molecular Crystals and Liquid Crystals, 35:3-4, 261-266

To link to this article: http://dx.doi.org/10.1080/15421407608083676

Mol. Cryst. Liq. Cryst., 1976, Vol. 35, pp. 261–266
© Gordon and Breach Science Publishers, Ltd., 1976
Printed in Holland

Evidence for a Phase Transition in Crystalline 2-3 Dimethyl 1-4 Naphthoquinone

M. BRETON, N. B. CHANH, J. HOUSTY
Laboratoire de Cristallographie et Physique Cristalline, Université de Bordeaux I (France)

and

D. LOUER
Laboratoire de Cristallochimie, Université de Rennes (France)

(*Received January 5, 1976*)

By means of X-Ray diffraction and differential microcalorimetry, 2-3 dimethyl 1-4 naptho-quinone crystal have been shown to be dimorphic with reversible thermal transition at 90°C. The crystal data of the monoclinic low temperature form (II) are known; those of the high temperature one (I) are obtained by an automatic indexing method of the powder diffraction pattern. The results show that form II corresponds to a substructure of form I in the direction of the *a* crystallographic axis while the *b* and *c* values are nearly the same.

INTRODUCTION

Some derivatives of 1-4 naphthoquinone present a disordered crystal structure at room temperature. On the other hand, this phenomenon exist only at higher temperature for other ones. The change from ordered to disordered structure is manifested through the presence of a characteristic thermal phase transition.[1] This work is a study of polymorphism in 2-3 dimethyl 1-4 naphthoquinone by means of X-ray diffraction, microcalorimetry and differential thermal analysis. The cell parameters for the high temperature form have been determined by means of an automatic indexing method of the powder diffraction pattern.

1 Crystal data of the room temperature form II (25°C)

At room temperature, the crystals of form II are monoclinic, space group $P2_1/n$ with:

$$
\begin{aligned}
a &= 7{,}520 \pm 0{,}005\ \text{Å}\\
b &= 8{,}350 \pm 0{,}005\ \text{Å}\\
c &= 14{,}970 \pm 0{,}010\ \text{Å}\\
\beta &= 91{,}80^\circ \pm 0{,}25^\circ\\
V &= 940\ \text{Å}^3
\end{aligned}
$$

with four molecules per unit cell, experimental density: 1.25, calculated density: 1.32. The structure determination[1] shows a special molecular packing. All the molecules are parallel to the *b* axis and stacked along the *a* axis. Contacts between the stacks are weak and correspond to distances slightly greater than Van der Waals distances.

2 Evidence of polymorphism

The X-ray diffraction study was performed on a polycrystalline sample in a closed cell by means of a Guinier Lenné camera. The diagram using CuKα radiation is shown in Figure 1. The modification at 90°C of the diffraction diagram corresponds to the transition into the high temperature form I.

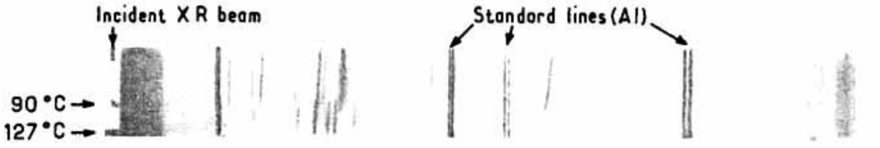

FIGURE 1 Guinier Lenné Camera pattern showing the crystalline phase change in 2-3 dimethyl 1-4 naphthoquinone.

The melting of this form occurs at 127°C when the diffraction peaks disappeared. Upon increasing the temperature, the differential thermal analysis curve (Figure 2a) showed two endothermic peaks, at 90°C and 127°C, corresponding to the two transitions respectively, upon lowering the temperature two exothermic peaks correspond to the reversible phase transformations: the first at 120°C (Liquid → Form I) with a delay of 7° and the second at 60°C (Form I → Form II) with a larger delay of 30° (Figure 2b).

Thus, 2-3 dimethyl 1-4 naphthoquinone exhibits a reversible transition in the solid state. The enthalpies of these different transitions were determined by means of differential microcalorimetry with the results:

$$\Delta H_{\text{form I} \leftrightarrow \text{form II}} = 600 \pm 20\ \text{cal/mole}$$

$$\Delta H_{\text{melting (form I)}} = 4100 \pm 100\ \text{cal/mole}$$

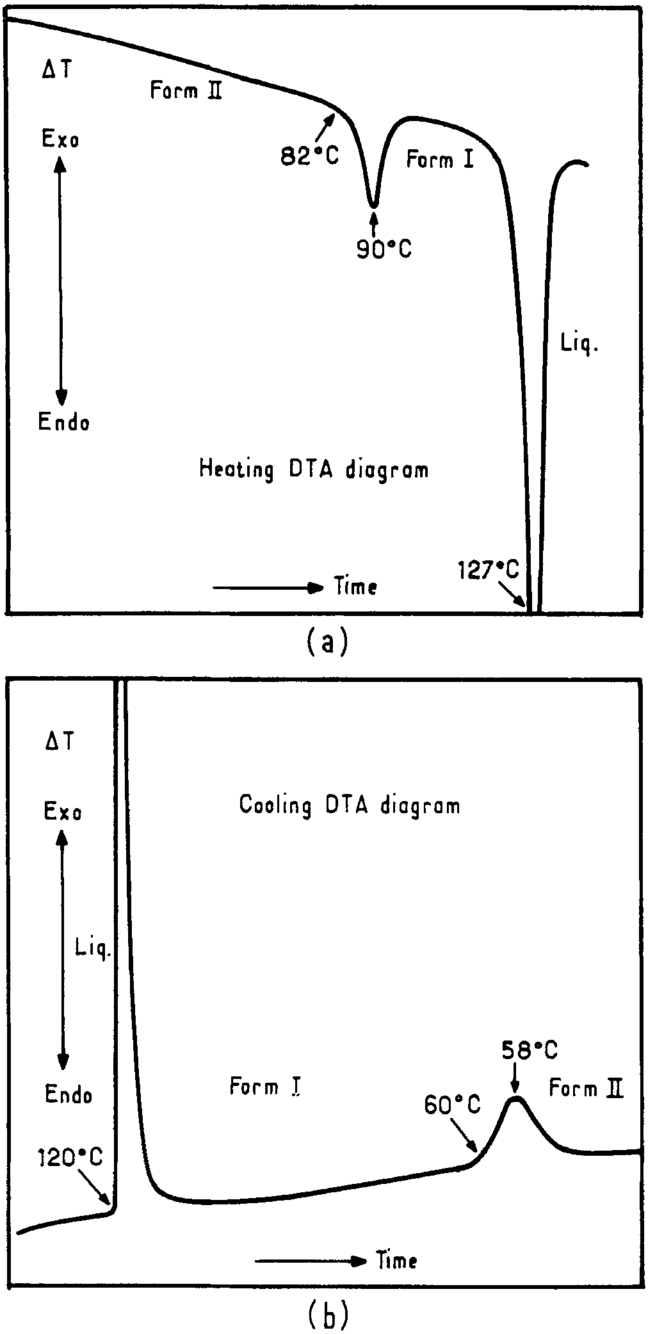

FIGURE 2 Thermograms of 2-3 dimethyl 1-4 naphthoquinone crystal.

3 Crystal data of the high temperature form I

In order to obtain a higher precision for the position, θ, of the diffraction peaks for the high temperature form, we recorded its spectrum with a powder diffractometer fitted with a heating system. The sample temperature was regulated to ±1°C. Positions of the peaks (with Kα, Cu radiation) were corrected by an internal standard (quartz) included in the sample. Taking into account the experimental difficulties inherent in the volatility of the product at the recording temperature, we chose a relatively fast scanning speed of $1°/5\ \mathrm{min}^{-1}$ in θ. Under these conditions, about fifteen reflections were observed; the maximum absolute error on the positions of the diffraction peaks is estimated to be 0.03° in the region studied.

In spite of these experimental difficulties and the small number of recorded reflections, we tried to find the symmetry and the cell parameters of the high temperature form I by using an automatic program for indexing the powder diffraction diagram based on the variations of the cell parameters by dichotomy.[2] A new version of program P1 with automatic indexing in systems of monoclinic or higher symmetry[3] led to the following solution, after refinement by least-squares,

FORM I $T = 105°\mathrm{C}$—orthorhombic system
$a = 4{,}000 \pm 0{,}006$ Å
$b = 8{,}356 \pm 0{,}020$ Å
$c = 14{,}674 \pm 0{,}020$ Å
$V = 490$ Å^3

TABLE I

X-Ray powder diffraction data of high temperature form (I) of 2-3 dimethyl, 1-4 naphthoquinone

$d_{\mathrm{meas.}}$	$d_{\mathrm{calcd.}}$	$h\ k\ l$	I/I_0
7.34	7.337	0 0 2	1.00
7.27	7.262	0 1 1	0.26
5.52	5.515	0 1 2	0.06
4.18	4.178	0 2 0	0.11
3.86	3.859	1 0 1	0.21
3.66	3.668	0 0 4	0.13
3.62	3.630	0 2 2	0.13
3.60	3.608	1 1 0	0.21
3.52	3.512	1 0 2	0.19
3.49	3.503	1 1 1	0.61
3.18	3.177	0 2 3	0.07
3.10	3.096	1 0 3	0.34
2.70	2.703	1 0 4	0.03
2.57	2.572	1 1 4	0.04
2.44	2.445	0 0 6	0.02

These data correspond to 2 molecules per cell, with a calculated density equal to 1.27. The interplanar spacings of Table I were calculated from these parameters.

CONCLUSION

We know that the crystalline cell parameters obtained by means of an automatic indexing method of powder diffraction diagrams must be considered carefully. The validity of the solution depends on the precision of the collected diffraction lines. The lines of our investigation show that the cell of the high temperature form I of 2-3 dimethyl 1-4 naphthoquinone derives from the low temperature one II by:

a change of the crystalline symmetry from monoclinic to orthorhombic upon increase of developed temperature;

a substructure in the *a* crystallographic direction, while the *b* and *c* values are nearly the same:

$$a(\mathrm{I}) \simeq a(\mathrm{II})/2$$
$$b(\mathrm{I}) \simeq b(\mathrm{II})$$
$$c(\mathrm{I}) \simeq c(\mathrm{II})$$

a decrease of the density from 1,32 (II) to 1,27 (I).

The observed transition does not seem to induce important modifications in the crystal structure, as evidenced by the relatively small values of the enthalpy of transition (600 cal-mole^{-1}). This transition probably involves reorientation motions of the molecules around the pseudo-binary axis perpendicular to the plane of the naphthoquinone ring. This interpretation would be consistent with the value of the transition entropy which, according to McCullough,[4] corresponds to a ratio of the number of molecular configuration in the two forms.[5,6] One should find:

$$\Delta S_{\text{conf}} = \frac{\Delta H_{\text{conf}}}{T_{\text{tr}}} = R \log \frac{N_1}{N_2} \rightarrow \frac{N_1}{N_2} = 2{,}2$$

A full study of this mechanism of the transition would require the knowledge of the crystal structure of the high temperature form I obtained from diffraction measurements on single crystals.

References

1. M. Breton, Thèse, Bordeaux (1972).
2. D. Louer and M. Louer, *J. Appl. Cryst.*, **5**, 271–275 (1972).
3. D. Louer. To be published.

4. John P. McCullough and E. F. Westrum, Jr., *Physics and Chemistry of the Organic Solid State*, Vol. I. eds. D. Fox, M. M. Labes, A. Weissberger, John Wiley and Sons, New York (1963).
5. N. B. Chanh, Y. Bouillaud, and P. Lencrerot, *J. Chim. Phys.*, **67**, no. 6, 1198 (1970).
6. N. B. Chanh and Y. Haget, *Acta Cryst.*, **B28**, 3400–3404 (1972).