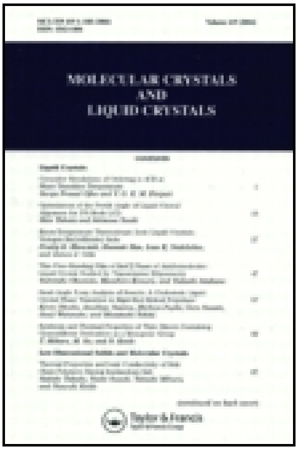


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Solid State Polymorphism of Some 4,4′-Disubstituted Phenylcyclohexanes

W. Haase [a] & R. Pendzialek [a]

[a] Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, Petersenstraβe 20, D-6100, Darmstadt, Federal Republic of Germany

Version of record first published: 17 Oct 2011.

To cite this article: W. Haase & R. Pendzialek (1983): Solid State Polymorphism of Some 4,4′-Disubstituted Phenylcyclohexanes, Molecular Crystals and Liquid Crystals, 97:1, 209-217

To link to this article: http://dx.doi.org/10.1080/00268948308073151

Mol. Cryst. Liq. Cryst., 1983, vol. 97, pp. 209–217
0026-8941/83/9704-0209/$18.50/0

Printed in the United States of America

Solid State Polymorphism of Some 4,4′-Disubstituted Phenylcyclohexanes[†]

W. HAASE and R. PENDZIALEK

Institut für Physikalische Chemie der Technischen Hochschule
Darmstadt, Petersenstraße 20, D-6100 Darmstadt
Federal Republic of Germany

(Received January 31, 1983)

The phase transitions and thermal properties of some mesogenic 4,4′-disubstituted phenylcyclohexanes (PCH) have been extensively studied using a differential scanning calorimeter and a polarizing microscope. The complex phase relation assumed for PCH 3 was unambiguously confirmed. Three distinct melting points of PCH 3 were observed and their conditions of individual occurrence determined. A further compound, PCH 7, showed an even more complicated melting behavior, namely four individual melting points. Their conditions of occurrence were also analyzed. The respective enthalpies of transition were determined using the DSC-method. The occurrence of solid state polymorphism and the reason for its existence are discussed for PCH 3.

I. INTRODUCTION

Many authors have reported on the solid state polymorphism of a large number of liquid crystalline substances since the observation of two solid phases for *p*-azoxyanisole (PAA) by Bernal and Crowfoot.[1] These reports either mentioned the occurrence of solid state transitions or to a lesser extent the appearance of more than one melting point. In some of the more recent papers[2–10] concerning solid state polymorphism in mesogenic compounds, it was shown that the occurrence, i.e. the formation of different solid modifications is dependent on the previous thermal treatment of the substance in question.

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

Although the thermal properties of some *trans*-4-n-alkyl-(4'-cyanophenyl)cyclohexanes (PCH) have previously been studied,[11,12] no particular evidence existed for solid crystalline polymorphism in the PCHs, although Eidenschink *et al.*[11] and Pohl *et al.*[12] first observed a melting temperature of 36°C for PCH 3. In a subsequent publication concerning this compound,[13] it was mentioned that the actual melting point is 42°C. In addition Eidenschink *et al.*[11] briefly hinted at the occurrence of another phase transition for PCH 7 at 17°C.

The results of our own work[14] on binary nematic mixtures consisting of various PCHs indicated a rather more complex melting behavior on the part of some of the components in the mixtures, as compared with the melting behavior of the pure compounds. These observations were restricted to systems that were either composed of PCH 3 or PCH 7. It was thus assumed that PCH 3 as well as PCH 7 could occur in more than two solid modifications. In order to gain an insight into the relationship between the thermal prehistory of some PCHs and their observed melting behavior in binary mixtures, it seemed necessary to conduct an extensive thermal analysis of the pure compounds.

2 EXPERIMENTAL

2.1 Samples

The compounds investigated were of the *trans*-4-n-alkyl-(4'-cyanophenyl) cyclohexane type $NC—C_6H_4—C_6H_{10}—R$ with R: C_3H_7—(PCH 3), C_5H_{11}—(PCH 5) and C_7H_{15}—(PCH 7), as well as of the *trans*-4-n-alkyl-(4'-alkoxyphenyl) cyclohexane type $R'—C_6H_4—C_6H_{10}—C_3H_7$ with R': C_2H_5O—(PCH 302) and C_4H_9O—(PCH 304).

The substances were obtained from E. Merck, Darmstadt. No further purification was carried out, as the purity of at least 99.8% as quoted by the manufacturer was in accord with our own observations. All samples were encapsulated in hermetically sealed aluminium sample pans. The mass of three individual samples per compound was determined with a Sartorius micro-balance with an accuracy of up to ±0.01 mg and varied from 2 to 6 mg. Prior to initial thermal analysis, all samples were heated up to their clearing point, subsequently cooled at 0.05°C/min to −6°C, and thereafter kept at this temperature for three days, utilizing a Lauda-Ultracryostat UK-60 SW in conjunction with the programmer P 120.

2.2 Apparatus

The calorimetric and thermal investigations were performed using a Du Pont 990 Thermal Analyzer in conjunction with the Differential Scanning Calorimeter Cell. The system was calibrated for thermal analysis with *p*-nitrotoluene, naphthalene, benzoic acid and adipic acid (Fisher Certified TherMetric Standards). For calorimetric work, the calibration was carried out utilizing indium as standard. The heating and cooling rates were controlled by employing liquid nitrogen. All DSC-measurements were performed in the heating mode at a rate of 2°C/min.

Besides determining all transition temperatures by the DSC-method, we also observed some of the transition points using a Leitz-Orthoplan-Pol Polarizing Microscope in conjunction with the Mettler hot stage FP-52 and control unit FP-5. The observations were likewise conducted in the heating mode at a rate of 0.2°C/min permitting an accuracy of ±0.1°C. The integration of the endothermic maxima was accomplished with a Haff-Planimeter with an error of ±0.01 in.^{2}

3 RESULTS AND DISCUSSION

3.1 Phase transitions of PCH 3

The systematic variation and subsequent application of different thermal treatments to the encapsulated compound within as well as without the DSC-cell now permit the unambiguous specification of three solid modifications of PCH 3. Thus, one finds the clearing point at 45.9°C and a melting point of a solid phase C_I at 42.7°C. In addition to this, two further solid modifications, namely C_{II} and C_{III}, melt at 35.6°C and 21.0°C respectively. The corresponding enthalpies of transition are to be found in Table I. The appropriate thermal treatments that give the three solid states independently of one another are as follows:

C_I: Commencing from the isotropic state the sample was stored at −6°C for 24 h.

C_{II}: Rapid cooling of the isotropic melt at a rate of 15–20°C/min to 5–10°C below the crystallization point.

TABLE I

Transition temperatures and transition enthalpies for PCH 3

Transition	Temperature [°C]	Enthalpy [kJ/mol]
N-I	$45.9 \pm 0.4^{a,b}$	0.7 ± 0.2
C_I-N	42.7 ± 0.3^{b}	19.0 ± 0.8
C_{II}-N	35.6 ± 0.4^{a}	12.8 ± 1.0^{a}
C_{III}-N	21.0 ± 0.6	13.4 ± 1.0

[a] Pohl *et al.*[12] reported $T_{N\text{-}I}$: 46°C; $T_{C\text{-}N}$: 36°C; $\Delta H_{C\text{-}N}$: 11.3 kJ/mol.
[b] Eidenschink[13] reported $T_{N\text{-}I}$: 46°C; $T_{C\text{-}N}$: 42°C.

C_{III}: Quenching of the isotropic liquid just up to the onset of crystallization and immediate interruption of the cooling process.

The typical DSC-thermograms of the melting processes of the three solid phases and the transition from the nematic phase to the isotropic liquid are depicted in Figure 1.

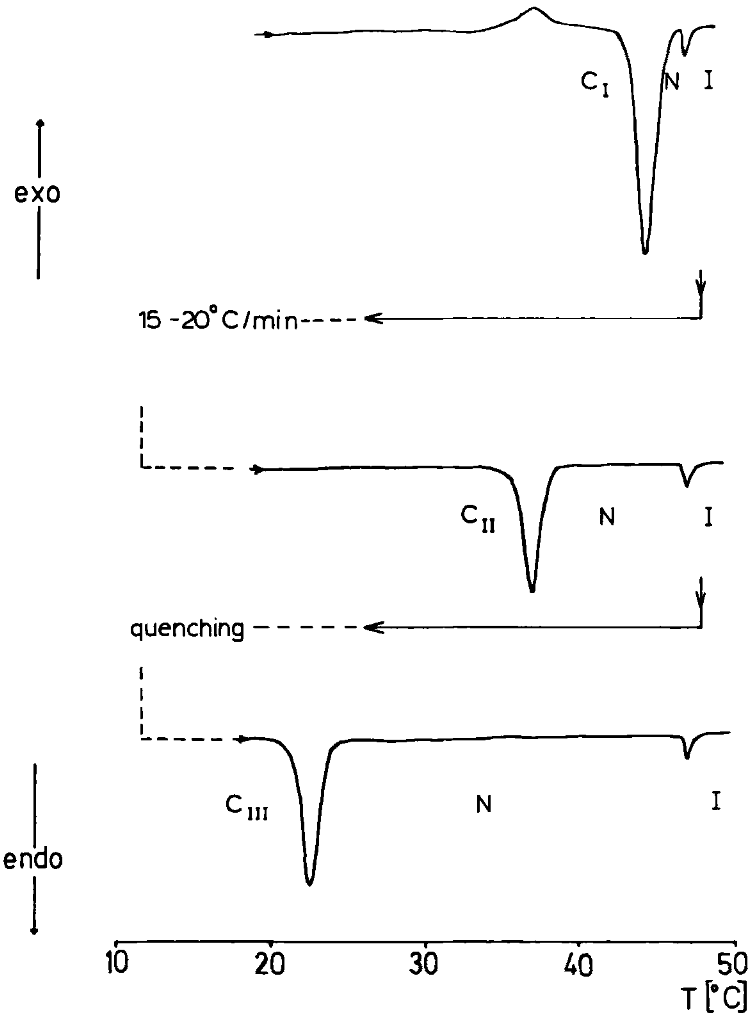


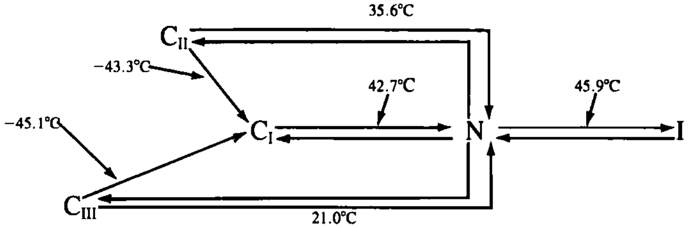
FIGURE 1 DSC-thermograms showing the effect of thermal treatment on the melting behavior of PCH 3.

Based on the assumption that the crystalline phases C_{II} and C_{III} represent thermodynamically metastable modifications of PCH 3 above −6°C, the investigations were extended to well below the crystallization temperature. The extensive thermal analysis by the DSC-method revealed two further endothermic transitions at −43.3°C and −45.1°C. These transitions did not occur concurrently but were, instead, dependent upon which metastable solid phase was brought to crystallization. In all cases when the solid state C_{II} occurred through appropriate thermal treatment and thereafter was cooled further to approximately −60°C, the DSC-traces (heating mode) showed a small endothermic transition at −43.3°C and subsequently over the remainder of the temperature range only a melting signal at 42.7°C. Likewise, in all instances when the solid phase C_{III} occurred, a small endothermic peak at −45.1°C was again followed only by a melting signal at 42.7°C. Based on these observations it should be concluded that the following phase transitions must have occurred:

$$C_{II} \xrightarrow{-43.3^\circ C} C_I$$

$$C_{III} \xrightarrow{-45.1^\circ C} C_I$$

Thus all the phase transitions that have thus far been observed can be rationalized by the following diagram



For an understanding of the behavior of the solid state polymorphism of PCH 3 the idealized free energy-temperature diagram in Figure 2 serves to clarify the relationship.

From the above-mentioned phase transitions of PCH 3 and from Figure 2 it follows that one is to expect a third solid state transition, namely $C_{III} \rightarrow C_{II}$. This has so far not been observed. This may be due to a very small enthalpy of transition being involved, making it difficult to ascertain from the DSC-traces whether a transition has actually taken place.

3.2 Phases of PCH 5

Extensive thermal analysis of PCH 5 revealed that this compound merely seems to exhibit a single transition behavior. This means that besides the

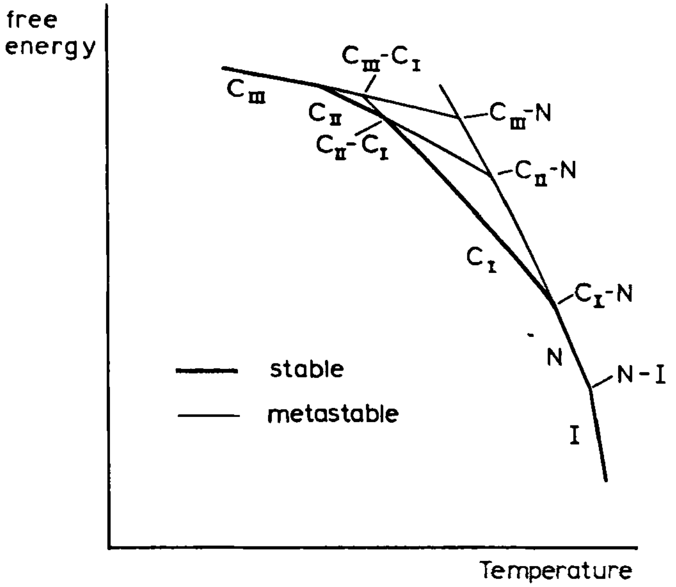


FIGURE 2 Idealized curve of free energy vs temperature for PCH 3.

clearing point and one melting point, no further transitions of any kind were observed. The transition temperatures and corresponding enthalpies are shown in Table II.

TABLE II

Transition temperatures and transition enthalpies for PCH 5

Transition	Temperature [°C]	Enthalpy [kJ/mol]
N-I	54.5 ±0.3[a]	0.9 ±0.2
C-N	28.9 ±0.6[a]	19.6 ±0.6[a]

[a] Pohl *et al.*[12] reported $T_{N\text{-}I}$: 55°C; $T_{C\text{-}N}$: 30°C; $\Delta H_{C\text{-}N}$: 18.0 kJ/mol.

3.3 Phases of PCH 7

As was to be expected, this compound presented a rather complicated phase behavior. Thus besides the nematic phase, a total of four different solid states can occur in PCH 7. The transition temperatures and their respective enthalpies are given in Table III.

The applied thermal treatment resulted in the occurrence of more than one solid phase in the majority of DSC-runs. It is therefore not yet possible to state the thermal conditions under which three of these phases, namely

TABLE III

Transition temperatures and transition enthalpies for PCH 7

Transition	Temperature [°C]	Enthalpy* [kJ/mol]
N-I	57.8 ±0.4[a]	1.0
C_I-N	30.0 ±0.4[a]	25.5[a]
C_{II}-N	17.1 ±0.5[b]	19.0
C_{III}-N	15.7 ±0.3	19.6
C_{IV}-N	11.3 ±0.4	19.6

[a] Pohl *et al.*[12] reported T_{N-I}: 59°C; T_{C-N}: 30°C; ΔH_{C-N}: 25.5 kJ/mol.
[b] Eidenschink *et al.*[11] mentioned a phase transition at 17°C.
*Standard deviations for the transition enthalpies cannot yet be quoted.

C_{II}, C_{III} and C_{IV}, will occur independently of one another. This is also the reason why standard deviations for the enthalpies of fusion are not included in the data. A selection of thermal treatments is given in Table IV to clarify the above-mentioned situation.

TABLE IV

A selection of thermal treatments applied to PCH 7 and the resultant solid phases observed in DSC-runs in the heating mode

Thermal treatment	Resultant phase(s)
Quenching until crystallization had occurred	C_{III} and some C_{II}
Quenching to well below crystallization	C_{III}
Quenching to a few degrees below crystallization	C_{II} and C_{IV}
Slow cooling from the nematic phase down to approx. 23°C, thereafter quenching to well below 0°C	Equal quantities of C_{II} and C_{III}

3.4 Phases of PCH 302 and PCH 304

The transition points and their respective enthalpies for both compounds are given in Table V. Some evidence exists that these compounds may also show solid state polymorphism, namely a solid-state transition at 24°C in PCH 302 and similarly at 25°C in PCH 304. Investigations to secure further data on this are presently being undertaken.

4 CONCLUSION

As a result of our investigations, which were concentrated upon clarifying the melting behavior of some PCHs, it seems reasonable to assume that the

TABLE V

Transition temperatures and transition enthalpies for PCH 302 and PCH 304

Transition		Temperature [°C]	Enthalpy [kJ/mol]
PCH	N-I	(37.8 ±0.3)	0.7 ±0.2
302	C-I	40.8 ±0.3	26.4 ±0.3
PCH	N-I	(33.0 ±0.4)	0.5 ±0.2
304	C-I	35.5 ±0.3	30.6 ±0.8

various solid states of a compound are attainable by means of an appropriate thermal treatment. The occurrence of solid state polymorphism, as for example in PCH 3 and PCH 7, and possibly in PCH 302 and PCH 304, as well as in various other types of mesogenic compounds, supports the assumption that this is the rule rather than the exception.

Detailed knowledge of the molecular structure and packing in the crystalline state of the solid phases observed is outstanding because the growth of single crystals and their X-ray examination has not yet been possible.

We nevertheless assume that the three solid modifications of PCH 3 are probably the result of different packing arrangements in the crystal because this compound in particular is not susceptible to any great changes in molecular structure in the conformational sense. This view is supported by the molecular structure of BCH30 and BCH5CN[15] who have geometrically equivalent molecular building blocks, which are also to be found in the PCHs.

Acknowledgments

We would like to thank the Deutsche Forschungsgemeinschaft for their financial support of this work. We are greatly indebted to Dr. R. Eidenschink of E. Merck, Darmstadt for supplying us with the samples, and we also wish to express our thanks to him for helpful discussions.

References

1. J. P. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933).
2. L. Bata, V. L. Broude, V. G. Fedotov, N. Kroo, L. Rosta, J. Szabon, L. M. Umarov and I. Vizi, *Mol. Cryst. Liq. Cryst.*, **44**, 71 (1978).
3. T. Hatakeyama and M. Ikeda, *Mol. Cryst. Liq. Cryst.*, **45**, 275 (1978).
4. N. Kirov, M. P. Fontana and F. Cavatorta, *Mol. Cryst. Liq. Cryst.*, **54**, 207 (1979).
5. J. Chruściel, L. Richter and M. Rachwalska, *Mol. Cryst. Liq. Cryst.*, **75**, 155 (1981).
6. N. Kirov, M. P. Fontana, F. Cavatorta and H. Ratajczak, *Mol. Cryst. Liq. Cryst.*, **75**, 303 (1981).
7. S. Miyajima, N. Nakamura and H. Chihara, *Mol. Cryst. Liq. Cryst.*, **87**, 41 (1982).
8. M. Yasuniwa and K. Minato, *Mol. Cryst. Liq. Cryst.*, **87**, 97 (1982).
9. S. C. Jain, S. A. Agnihotry and V. G. Bhide, *Mol. Cryst. Liq. Cryst.*, **88**, 281 (1982).
10. K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, **90**, 85 (1982).

11. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem.*, **89**, 103 (1977).
12. L. Pohl, R. Eidenschink, J. Krause and D. Erdmann, *Phys. Lett.*, **60A**, 421 (1977).
13. R. Eidenschink, *Kontakte (Merck)* 1979 (1), 15.
14. W. Haase and R. Pendzialek, 10.Freiburger Arbeitstagung Flüssigkristalle, Freiburg/Br. (1980) and to be published.
15. W. Haase, H. Paulus and H.-T. Müller, *Mol. Cryst. Liq. Cryst.* **97**, 131 (1983).