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Liquid-crystalline reference compounds

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Liquid-crystalline reference compounds

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A polar (PCH-5) and a non-polar (I52) compound are introduced as liquid-crystalline bench-mark compounds. The materials chosen are affordable, stable, easy to handle and possess nematic mesophases between 30–54·9 and 24–103·4°C. All relevant macroscopic physical properties, such as refractive indices n_o and n_e, dielectric permittivities $\varepsilon_\parallel$ and $\varepsilon_\perp$, elastic constants K_{11}, K_{22} and K_{33}, and bulk and rotational viscosities are given as a function of temperature, wavelength and frequency, when applicable. The reference compounds are available from E. Merck, Darmstadt.

1. Introduction

The rapid progress in the field of liquid crystal research and application has led to an increasing effort to obtain accurate physical data for a wide range of substances. Today it is often difficult to compare and evaluate material parameters which were obtained in different laboratories with different instrumentation.

In many experiments *N*-(4-methoxybenzylidene)-4′-*n*-butylaniline (MBBA) has been used as a reference [1, 2]. However, due to its sensitivity to water it may decompose and exhibit a clearing point anywhere between 47°C and about 35°C. Clearly, this drawback eliminates MBBA as a potential bench-mark compound. Another compound proposed is *p*-azoxyanisole (PAA) [2], but due to its instability with regard to radiation this material offers no real alternative.

In 1978 Demus [3] provided an extensive characterization and discussion of 4-nitrophenyl-4′-*n*-octyloxybenzoate (NPOOB), followed in 1983 by a comparable contribution for 4-*n*-hexoxyphenyl-4′-*n*-decycloxybenzoate (HOPDOB) [4]. The scope of these investigations was primarily to provide experimentalists and theoreticians with substances to study various intrinsic effects of liquid-crystalline materials, particularly in the higher ordered phases. In the present contribution we intend primarily to establish a means for instrumental calibration. For this reason we have sought single compounds which have: a nematic mesophase at ambient temperature; a suitable melting point in order to perform a repurification easily (if necessary); sufficient stability in response to heat, radiation and moisture; and the ability to be oriented easily in test cells in order to avoid additional errors.

After an evaluation of various compounds we have chosen two compounds for this purpose and present an extensive set of physical data of the polar compound 4-(*trans*-4′-pentylcyclohexyl)-benzonitrile (PCH-5) and the non-polar compound 4-ethyl-2-fluoro-4′-[2-(*trans*-4-*n*-pentylcyclohexyl)-ethyl]-biphenyl (I52) intended as liquid-crystalline bench-mark compounds for both instrumental calibration and research purposes (see figure 1). PCH-5 was first described by Eidenschink and co-workers [5, 6] and satisfies most of the criteria given here. I52 was chosen for its exceptionally wide nematic range, resulting in small derivatives of the physical quantities in respect to temperature. It was introduced by Balkwill and co-workers [7, 8].

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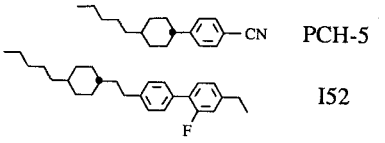

Figure 1. Structure of PCH-5 and I52.

2. General properties

The main characteristics of PCH-5 and I52 are given in tables 1 and 2. The melting and clearing points are the temperatures for the first optical change observed at the transition, e.g. as determined with a Mettler oven, or a hot stage under a polarizing microscope. The melting point should be correct to within ± 1 K, the clearing point to $\pm 0{\cdot}2$ K. Both compounds can be supercooled below their melting point to some extent once they are in the nematic phase. The corresponding melting and clearing enthalpies are correct to within $\pm 80\,\mathrm{J\,mol^{-1}}$. However, the melting enthalpy depends strongly on the particular crystalline state present in the solid and may vary considerably, depending on the history of the sample. Clearly, the quoted melting enthalpy should *not* be used for calorimetric reference purposes. The purity of the substances investigated as determined by standard techniques (H.P.L.C. and the van't Hoff relation by employing D.S.C.) is also given in tables 1 and 2.

Table 1. General properties of PCH-5.

Compound name	4-(*trans*-4′-*n*-pentylcyclohexyl)-benzonitrile (PCH-5)
Phase transitions	C → 30°C → N → 54·9°C → I
Melting point	+30°C
Clearing point	+54·9°C
Melting enthalpy	21·35 kJ mol^{-1}
Clearing enthalpy	0·96 kJ mol^{-1}
Molecular weight	255·4
Purity D.S.C.	100 per cent
H.P.L.C.	99·8 per cent

Table 2. General properties of I52.

Compound name	4-Ethyl-2-fluoro-4′-[2-(*trans*-4-*n*-pentylcyclohexyl)-ethyl]-biphenyl (I52)
Phase transitions	C → 24°C → S_B → (13°C) → N → 103·4°C → I
Melting point	+24°C
Clearing point	+103·4°C
Melting enthalpy	14·23 kJ mol^{-1}
Clearing enthalpy	1·34 kJ mol^{-1}
Molecular weight	380·6
Purity D.S.C.	99·7 per cent
H.P.L.C.	98·7 per cent

We now give many physical parameters as a function of temperature, wavelength or frequency, when applicable. For the non-polar liquid crystal I52, a determination of the elastic constants was not possible with our instrumentation, since the small resulting value of $\Delta\varepsilon$ did not allow us to obtain electrical deformations. All data were measured and compiled with the greatest possible care. In particular, various

cross-checks have been performed in order to ensure that the temperature scale used for this investigation by the various instruments was correct.

3. Physical properties at ambient temperature

In tables 3 and 4 the viscous, optical, dielectric, elastic and diamagnetic properties of both PCH-5 and I52 are given at 20 and 25°C. (Having the sample at 25°C, slightly above room temperature, will usually avoid the condensation of moisture.)

3.1. *Bulk viscosity*

The viscosity given is the kinematic viscosity of the bulk material without having the director aligned in a specific orientation. A simple Ostwald-type viscosimeter was used for this purpose. (The kinematic viscosity ν is related to the corresponding dynamic viscosity η by $\nu = \eta/\varrho$, where ϱ is the density of the material.) The error in ν is of the order of $\pm 0{\cdot}3\,\mathrm{mm^2\,s^{-1}}$.

3.2. *Rotational viscosity*

The rotational viscosity, γ_1, was determined by Schneider at the University of Siegen with an instrumental set-up described by Kneppe and Schneider [9]. The error for γ_1 is estimated to be $\pm 1{\cdot}5$ per cent.

3.3. *Optical anisotropy*

The refractive indices n_o and n_e were obtained using an Abbe refractometer and suitable light sources (a mercury vapour lamp with narrow band filters, a sodium vapour lamp, and a He–Ne laser). For the measurements some material was deposited on the prism of the refractometer which had been treated with a lecithin solution in order to achieve homeotropic alignment. The indices are correct to within $\pm 0{\cdot}0004$. A method for the interpolation of the refractive indices at arbitrary wavelengths within the given range is described in §5.

3.4. *Dielectric anisotropy*

For the measurement of the dielectric permittivities the liquid crystal was placed in separate test cells having planar and homeotropic alignment. When the capacitance of both the empty and filled cell is known we may easily obtain $\varepsilon_\parallel$ and $\varepsilon_\perp$. The main source of error stems from the existence of regions with degraded orientation in the cells and could possibly amount to $\pm 0{\cdot}2$. As can be seen from table 4, it is obvious that I52 does not possess a significant dielectric anisotropy. It is well justified to assign a $\Delta\varepsilon$ of 0 for this compound. The dielectric anisotropy is also a function of the frequency. At a temperature of 25°C, figure 2 gives $\varepsilon_\parallel$ and $\varepsilon_\perp$ of PCH-5 in the frequency range between 10 Hz and 50 kHz. A comparable diagram for the non-polar compound I52 is not appropriate.

3.5. *Elastic constants*

The elastic constants have been determined by evaluating the director deformations induced by electric and magnetic fields in specific test cells [1]. A modified experimental set-up as described by Scheuble [10] was used. The error of the elastic constants is less than $0{\cdot}3 \times 10^{-12}\,\mathrm{N}$.

Table 3. Physical properties of PCH-5 at 20 and 25°C.

Property			20°C					25°C		
Density, ϱ/g cm^{-3}			0·9706					0·9669		
Bulk viscosity, ν/mm^2 s^{-1}			22·5					17·9		
Rotational viscosity, γ_1/Pa s			0·1507					0·1119		
Optical anisotropy	436 nm	509 nm	546 nm	589 nm	633 nm	436 nm	508 nm	546 nm	589 nm	633 nm
Δn	0·1360	0·1275	0·1249	0·1227	0·1208	0·1370	0·1255	0·1224	0·1205	0·1186
n_e	1·6408	1·6229	1·6173	1·6122	1·6080	1·6408	1·6194	1·6137	1·6089	1·6049
n_o	1·5048	1·4954	1·4924	1·4895	1·4872	1·5038	1·4939	1·4913	1·4884	1·4863
Dielectric anisotropy (1 kHz)										
$\Delta\varepsilon$			12·7					12·5		
$\varepsilon_\parallel$			17·5					17·4		
$\varepsilon_\perp$			4·8					4·9		
Elastic constants										
$K_{11}/10^{-12}$ N			9·6					9·1		
$K_{22}/10^{-12}$ N			6·5					5·3		
$K_{33}/10^{-12}$ N			19·4					17·9		
K_{33}/K_{11}			2·03					1·97		
K_{33}/K_{22}			3·0					3·4		
Diamagnetic anisotropy, $\Delta\chi/10^{-8}$			4·0					4·0		

Table 4. Physical properties of I52 at 20 and 25°C.

Property	20°C					25°C				
Density, ϱ/g cm^{-3}			1·0073					1·0038		
Bulk viscosity, ν/mm^2 s^{-1}			31·8					25·1		
Rotational viscosity, γ_1/Pa s			0·3307					0·2620		
Optical anisotropy	436 nm	509 nm	546 nm	589 nm	633 nm	436 nm	508 nm	546 nm	589 nm	633 nm
Δn	0·1673	0·1540	0·1494	0·1459	0·1431	0·1653	0·1524	0·1479	0·1443	0·1415
n_e	1·6881	1·6641	1·6563	1·6495	1·6443	1·6841	1·6610	1·6533	1·6466	1·6414
n_o	1·5208	1·5101	1·5069	1·5036	1·5012	1·5188	1·5086	1·5054	1·5023	1·4999
Dielectric anisotropy (1 kHz)										
$\Delta\varepsilon$			−0·06					−0·06		
$\varepsilon_\parallel$			2·976					2·964		
$\varepsilon_\perp$			3·038					3·024		

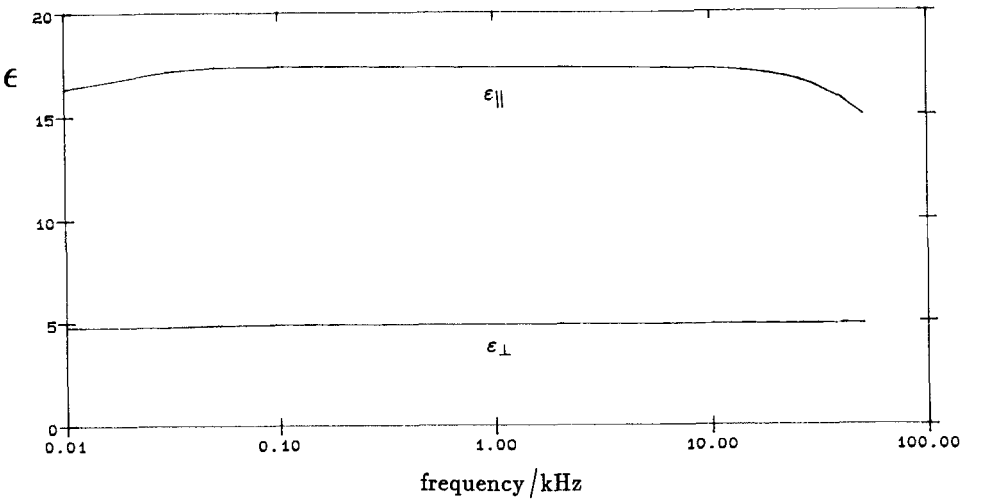

Figure 2. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of PCH-5 between 10 Hz and 50 kHz at 25°C.

3.6. *Diamagnetic anisotropy*

This quantity was not obtained in a separate experiment, but as a by-product in the form of an additional fitting parameter during the evaluation of the elastic constants. The error of the quoted value for $\Delta\chi$ is $\pm 0{\cdot}5$.

4. Physical properties at reduced temperatures

For many applications it is sufficient to consider the behaviour of liquid crystals at ambient temperature. However, when investigations of the materials regarding physical effects are made, measurements are performed at well defined reduced temperatures, T/T_{NI}. In order to facilitate a comparison of material properties at a certain given T_{red}, the physical parameters are given at T_{red} of 0·900, 0·925, 0·950 and 0·975 in tables 5 and 6.

5. Calculation of refractive indices according to the Cauchy formula

A most convenient way to describe the dependence of the refractive indices n_o and n_e on the wavelength is the application of the Cauchy formula, e.g. as explained by Wu [11]. The functional dependence of n_o and n_e on wavelength can be approximated to a high degree of accuracy by the expression

$$n_{o,e} = n_{\infty_{o,e}} + \frac{a_{o,e}}{\lambda^2} + \frac{b_{o,e}}{\lambda^4}.$$

In table 7 these three coefficients are given for both 20 and 25°C. The use of three coefficients improved the accuracy considerably; it would have also been possible to perform the fit with two terms, giving different parameters resulting in a slightly inferior fit. All three terms in the expansion should be used here, as the omission of the third would lead to incorrect results.

6. Summary and outlook

In the context of this investigation many determinations of the physical parameters of PCH-5 and I52 have been performed. Although we feel that this initial

Table 5. Physical properties of PCH-5 at several reduced temperatures.

Property	$T_{red} = 0{\cdot}900$ (22·1°C)		$T_{red} = 0{\cdot}925$ (30·3°C)		$T_{red} = 0{\cdot}950$ (38·5°C)		$T_{red} = 0{\cdot}975$ (46·7°C)	
Density, ϱ/g cm^{-3}	0·9690		0·9630		0·9565		0·9496	
Bulk viscosity, ν/mm^2 s^{-1}	20·4		14·5		11·0		8·9	
Rotational viscosity, γ_1/Pa s	0·1337		0·0832		0·0532		0·0326	
Optical anisotropy	589 nm	633 nm	589 nm	633 nm	589 nm	633 nm	589 nm	633 nm
Δn	0·1215	0·1196	0·1165	0·1150	0·1093	0·1079	0·0989	0·0976
n_e	1·6105	1·6064	1·6040	1·6001	1·5956	1·5919	1·5849	1·5812
n_o	1·4890	1·4868	1·4875	1·4851	1·4863	1·4840	1·4860	1·4836
Dielectric anisotropy (1 kHz)								
$\Delta\varepsilon$	12·7		12·1		11·3		10·2	
$\varepsilon_\parallel$	17·5		17·1		16·6		15·9	
$\varepsilon_\perp$	4·8		5·0		5·3		5·7	
Elastic constants								
$K_{11}/10^{-12}$ N	9·3		8·5		7·3		5·9	
$K_{22}/10^{-12}$ N	5·7		5·1		4·5		3·9	
$K_{33}/10^{-12}$ N	18·6		16·2		13·2		9·9	
K_{33}/K_{11}	2·00		1·91		1·80		1·67	
K_{33}/K_{22}	3·3		3·2		2·9		2·5	
Diamagnetic anisotropy, $\Delta\chi/10^{-8}$	4·0		3·9		3·7		3·4	

Table 6. Physical properties of I52 at several reduced temperatures†

Property	T_{red} = 0·900 (65·8°C)		T_{red} = 0·925 (75·2°C)		T_{red} = 0·950 (84·6°C)		T_{red} = 0·975 (94·0°C
Density, ϱ/g cm^{-3}	0·9753		0·9685		0·9617		0·9543
Bulk viscosity, ν/mm^2 s^{-1}	7·1		5·8		4·9		4·2
Rotational viscosity, γ_1/Pa s	0·0563		0·0417		0·0305		0·0211
Optical anisotropy	589 nm	633 nm	589 nm	633 nm	589 nm	633 nm	
Δn	0·1277	0·1253	0·1222	0·1200	0·1146	0·1127	
n_e	1·6197	1·6149	1·6122	1·6074	1·6031	1·5986	
n_o	1·4920	1·4896	1·4900	1·4874	1·4885	1·4859	
Dielectric anisotropy (1 kHz)							
$\Delta\varepsilon$	−0·02		0·0		+0·07		
$\varepsilon_\parallel$	2·861		2·837		2·813		
$\varepsilon_\perp$	2·881		2·841		2·739		

† Some measurements could not be performed at T_{red} = 0·975 because of the high clearing point of 103·4°C for I52.

Table 7. Cauchy coefficients of $n_{o,e} = n_{\infty_{o,e}} + (a_{o,e}/\lambda^2) + (b_{o,e}/\lambda^4)$ for I52 and PCH-5 at 20 and 25°C.

	I52				PCH-5			
Temperature/°C	20		25		20		25	
Refractive index	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
Cauchy coefficient								
n_∞	1·6173	1·4880	1·6132	1·4867	1·5868	1·4743	1·5939	1·4764
a/nm^2	8415	4434	9320	4576	6972	4646	523	2888
b/nm^4 10^8	9·588	3·408	7·912	2·897	6·254	2·198	15·95	4·394

coverage is fairly complete, we can think of an even more extensive approach. Other measurements have been carried out, the results of which are not shown here. If the reader is interested in more specific data obtained at different temperatures, wavelengths, frequencies, etc., than those quoted here, he or she is strongly encouraged to contact the authors.

Both PCH-5 and I52 are available upon request from E. Merck, Darmstadt, F.R. Germany. From several production batches of the specific compounds one has been selected and is exclusively reserved for bench-mark applications.

Provided that the scientific community finds that there is a further need to carry out a more extensive determination of the parameters described here, or extend the coverage to other quantities not discussed, we are open to further suggestions and are prepared to support actions undertaken in this respect.

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