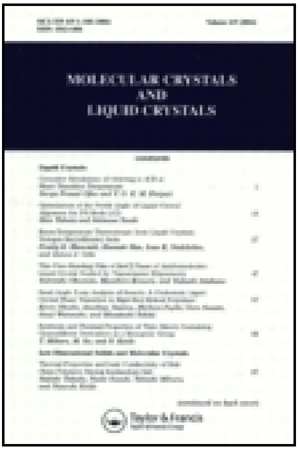

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Smectic Polymorphism of Some Bis-(4,4′-n-alkoxybenzylidene)-1,4-phenylenediamines up to 3 kbar by Differential Thermal Analysis (DTA). II†

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The *T-p* phase diagrams of the butoxy (BOBPD), the dodecoxy (DDOBPD), the tridecoxy (TRIDOBPD) and the tetradecoxy (TETDOBPD) homologues of the bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamine series have been determined up to 3 kbar and in the temperature range 300 K to 600 K by high pressure differential thermal analysis (DTA).

BOBPD exhibits only the nematic liquid crystalline phase at atmospheric pressure, whereas each of the three higher homologues additionally shows four smectic phases. With increasing pressure the number of smectic phases diminishes and the low temperature smectic phases, smG and smJ, vanish at higher pressure. TRIDOBPD and TETDOBPD do not exhibit any nematic phase at atmospheric pressure, but a pressure induced (probably nematic) phase appears for both substances under pressure. The nematic temperature range always increases with increasing pressure.

The complex behaviour of the smectic phases is discussed on a molecular point of view, where the interlayer forces are suggested to determine the different behaviour of low- and high-ordered smectic phases.

INTRODUCTION

During the last years the influence of high pressures on the phase behaviour of mesomorphic phases has become to play an important role in the field of liquid crystal investigations.[1]

The present high pressure measurements continue earlier experiments of

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†Part 1: Ref. 2

Spratte and Schneider[2] in order to improve the knowledge and understanding especially about smectic liquid crystalline phases. For the experiments four members of the homologous series of the bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamines have been used: the butoxy (BOBPD), the dodecoxy (DDOBPD), the tridecoxy (TRIDOBPD) and the tetradecoxy (TETDOBPD) compounds, respectively. These substances have been chosen following the work of Spratte and Schneider[2] who investigated the pentoxy, the hexoxy, the heptoxy and the octoxy homologues.

These substances exhibit several mesomorphic phases at atmospheric pressure (e.g. for the heptoxy homologue six smectic and the nematic phases have been found[3]) and thus information about different smectic phases could be obtained in a single experiment. Additionally some of these smectic phases have been found for the first time as has been verified by Barrall, Goodby and Gray[3] who named them smJ and smK.

EXPERIMENTAL

a. Apparatus and experimental procedure

For the measurements a high pressure differential thermal analysis equipment has been used. The experimental set up and the autoclave are described elsewhere.[2,4]

For the high pressure investigations the substances were encapsuled in a lead cell.[5] The main part of the measurements were performed with linear heating rates of 2 K min^{-1}. Smaller heating rates down to 0.2 K min^{-1} were used to evaluate the temperatures of those transitions which were less than 5 K apart from each other. The n/l transition temperatures of DDOBPD, TRIDOBPD and TETDOBPD have been determined sometimes in cooling runs, too.

At atmospheric pressure additional measurements in platinum cells have been carried out to determine the transition enthalpies ΔH. These results have been approved by differential scanning calorimetry (DSC).

Further experimental details are described in references.[2,4,5]

b. Accuracy

The accuracy of temperature measurements is better than ±0.5 K at room temperature and ±1 K at 600 K. The accuracy of the pressure determination is within ±5 bar. For transition enthalpies above 2 kJ mol^{-1} the accuracy is ±10% and for smaller ΔH values ±20%. The volume changes ΔV are within ±15% and ±30% respectively according to the accuracy of the ΔH values and of the initial slopes of the $T(p)$ transition lines.

c. Substances

The bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamines were synthesized from the corresponding 4-*n*-alkoxybenzaldehydes and 1,4-phenylenediamine

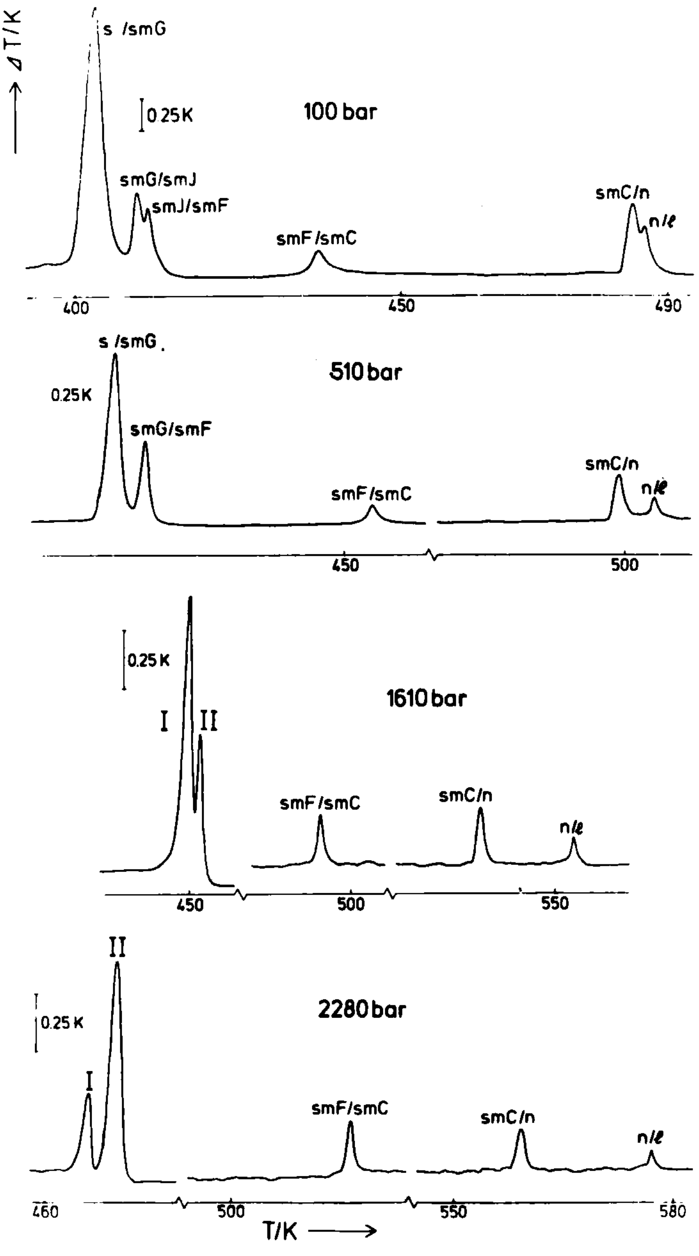

FIGURE 1 Original DTA traces of bis-(4,4′-*n*-dodecoxybenzylidene)-1,4-phenylenediamine (DDOBPD) at four different pressures

TABLE I

Phase transition temperatures T of the butoxy (BOBPD) and the dodecoxy (DDOBPD) homologues of the bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamines as a function of pressure p: coefficients of the polynomials $T/K = a + b\,(p/\text{bar}) + c\,(p/\text{bar})^2$

transition	a	$b \cdot 10^3$	$c \cdot 10^6$	pressure range
		BOBPD		
*s*1/*s*2	391.7	26.8	− 2.7	1–3000
*s*2/*n*	457.2	40.4	− 2.4	60–3000
n/*I*	563.7	89.9	−20.8	1– 500
		DDOBPD		
s/*smG*	394.7	39.5	− 4.5	1–1270
I	393.8	38.7	− 3.3	1320–3000
II	382.9	49.5	− 5.2	1320–3000
smG/*smJ*	404.1	33.8	−11.2	1– 480
smG/*smF*	404.1	30.1	− 2.9	480–1270
smJ/*smF*	406.5	34.0	−22.3	1– 480
smF/*smC*	429.9	44.9	− 2.9	1–3000
smC/*n*	477.1	41.2	− 2.8	1–3000
n/*I*	478.4	51.1	− 3.8	1–3000

TABLE II

Phase transition temperatures T of the tridecoxy (TRIDOBPD) and the tetradecoxy (TETDOBPD) homologues of the bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamines as a function of pressure p : Coefficients of the polynomials $T/K = a + b\,(p/\text{bar}) + c\,(p/\text{bar})^2$

transition	a	$b \cdot 10^3$	$c \cdot 10^6$	pressure range
		TRIDOBPD		
s/*smG*	399.1	40.7	− 9.8	1– 345
s/*smF*	402.5	25.8	5.6	345– 780
I	402.2	31.9	− 2.1	780–3000
II	399.5	36.2	− 2.6	780–3000
smG/*smJ*	402.3	31.4	− 7.4	1– 225
smG/*smF*	403.3	25.1		225– 345
smJ/*smF*	403.3	24.6		1– 225
smF/*smC*	427.1	43.8	− 2.5	1–3000
smC/*I*	472.5	41.5	5.7	1– 290
smC/*n*	473.6	40.2	− 2.5	290–3000
n/*I*	471.5	48.4	− 3.5	290–3000
		TETDOBPD		
s/*smG*	396.6	44.9	−27.4	1– 245
s/*smF*	398.9	28.3	1.4	245– 915
I	400.1	29.5	− 1.3	915–3000
II	396.0	35.2	− 2.3	915–3000
smG/*smJ*	399.0	34.9	−41.6	1– 185
smG/*smF*	397.8	33.3		185– 245
smJ/*smF*	400.2	20.7		1– 185
smF/*smC*	425.2	43.3	− 2.5	1–3000
smC/*I*	469.0	41.2	− 0.2	1– 680
smC/*n*	473.0	36.1	− 1.7	680–3000
n/*I*	468.7	43.2	− 2.7	680–3000

as described by Gray *et al.*[6] The 4-*n*-alkoxybenzaldehydes were synthesized from 4-hydroxybenzaldehyde and the corresponding *n*-alkylbromide with potassium hydroxide in dimethylformamide.[7] The four substances were recrystallized several times from benzene until no further change in the *n*/*l* phase transition temperature could be observed.

RESULTS

Figure 1, represents typical DTA traces of DDOBPD at four different pressures. About 50 runs have been performed to construct each *T*-*p* phase diagram. The transition temperatures of only some selected runs are plotted versus pressure in Figures 2–5. All *T*-*p* curves have been fitted to a quadratic form, $T/K = a + b\,(p/\text{bar}) + c\,(p/\text{bar})^2$; the three constants *a*, *b* and *c* are given in Tables I and II.

From the slopes $(dT/dp)_{\text{coex}}$ of the transition curves and the enthalpy changes ΔH the volume changes ΔV of the transitions have been deduced at 1 bar using the Clapeyron equation. These data are given in Table III.

The symbols used to designate the different phases are as follows: *s* for solid, *n* for nematic, *sm* for smectic and *l* for isotropic liquid; different solid and smectic phases are distinguished by numbers or capital letters.

TABLE III

Thermodynamic data for the butoxy (BOBPD), the dodecoxy (DDOBPD), the tridecoxy (TRIDOBPD) and the tetradecoxy (TETDOBPD) homologues of the bis-(4,4'-*n*-alkoxybenzylidene)-1,4-phenylenediamines at 1 bar

substance	transition	$\Delta H/kJ\ \text{mol}^{-1}$	$\Delta V/\text{cm}^3\ \text{mol}^{-1}$
BOBPD	*s1*/*s2*	2.5	1.7
	s2/*s3*	6.8	6.2
	s3/*n*	28.9	26.4
	n/*l*	1.5	2.5
DDOBPD	*s*/*smG*	40.1	41.1
	smG/*smJ*	6.5	5.3
	smJ/*smF*	3.3	2.0
	smF/*smC*	2.2	2.3
	smC/*n*	6.9	6.0
	n/*l*	2.2	2.3
TRIDOBPD	*s*/*smG*	57.3	58.4
	smG/*smJ*	6.3	4.9
	smJ/*smF*	3.0	1.8
	smF/*smC*	3.1	3.2
	smC/*l*	11.3	9.9
TETDOBPD	*s*/*smG*	55.7	62.9
	smG/*smJ*	5.3	4.6
	smJ/*smF*	4.0	2.1
	smF/*smC*	3.2	3.3
	smC/*l*	11.7	10.3

DISCUSSION

The phase transition temperatures at atmospheric pressure are in good agreement with those of Arora *et al.*[8]

The phases *sm*1 and *sm*3 in the paper of Spratte and Schneider[2] that could not be identified by these authors have been shown to be *smH* and a new smectic phase, *smJ*, respectively.[3] The smectic *B* phase of these authors has been identified to be *smF* by Barrall II *et al.*;[3] according to recent results of Goodby,[9] however, this phase could also be another new smectic phase, *smI*. In the present paper the notation *smF* is used.

With increasing pressure the number of smectic phases diminishes. So for DDOBPD (Figure 2) the *smJ* phase vanishes at a triple point *smG*/*smJ*/*smF*, that involves smectic phases only, at about 480 bar and 418 K and the *smG* phase at another triple point *s/smG/smF* at about 1270 bar and 438 K. An interesting aspect of the *T-p* phase diagrams is the decreasing stability range of all smectic phases except the *smF* phase with increasing pressure; in fact the temperature range of the smF phase is 23.1 K at 1 bar and 54 K at 3 kbar. A similar stabilization effect of high pressure has been found for the nematic phase; here the temperature range is 1.1 K at 1 bar and increases up to 22 K at 3 kbar.

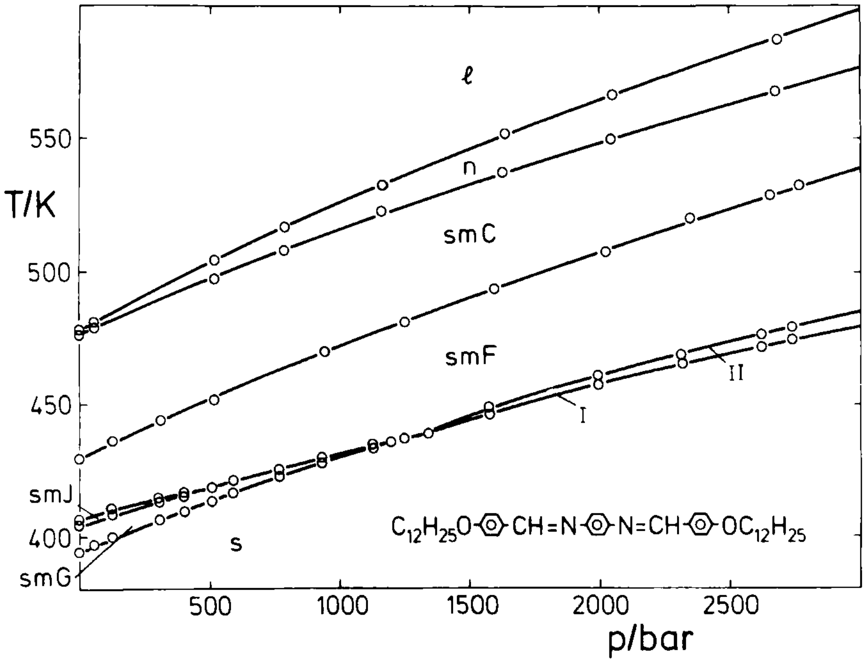

FIGURE 2 *T-p* phase diagram of bis-(4,4'-*n*-dodecoxybenzylidene)-1,4-phenylenediamine (DDOBPD)

During the experiments two endothermal transitions were observed above about 1320 bar and 439 K. These have been denoted as I and II in Figure 1 and also in Figures 2–4. The unusual feature observed is that the ratio of the peak areas of the I and II transitions varied with each new measurement (even at constant pressure) when the substance was heated from below the transition line I. This is demonstrated in Figure 1 considering the I and II transition peaks in the DTA runs at 1610 and 2280 bar respectively. The sum of the peak areas of the transitions I and II, however, was found to be constant within the experimental accuracy. It is difficult to explain these experimental results on the basis of only DTA investigations.

To our knowledge TRIDOBPD (Figure 3) has been investigated for the first time even at atmospheric pressure. At 1 bar four smectic phases but no nematic phase have been observed. The smectic phases show the same behaviour as for DDOBPD. The *smJ* and the *smG* phases vanish with increasing pressure at triple points *smG*/*smJ*/*smF* at about 225 bar and 409 K and *s*/*smG*/*smF* at about 345 bar and 412 K, respectively. The temperature range of the *smF* phase increases from 23.7 K at 1 bar up to 51 K at 3 kbar. Again two transitions I and II exist at pressures above ca. 780 bar and at temperatures above 427 K. A new phase appears at about 290 bar and 485 K.[13] This new phase was supposed to be the nematic phase taking into account that

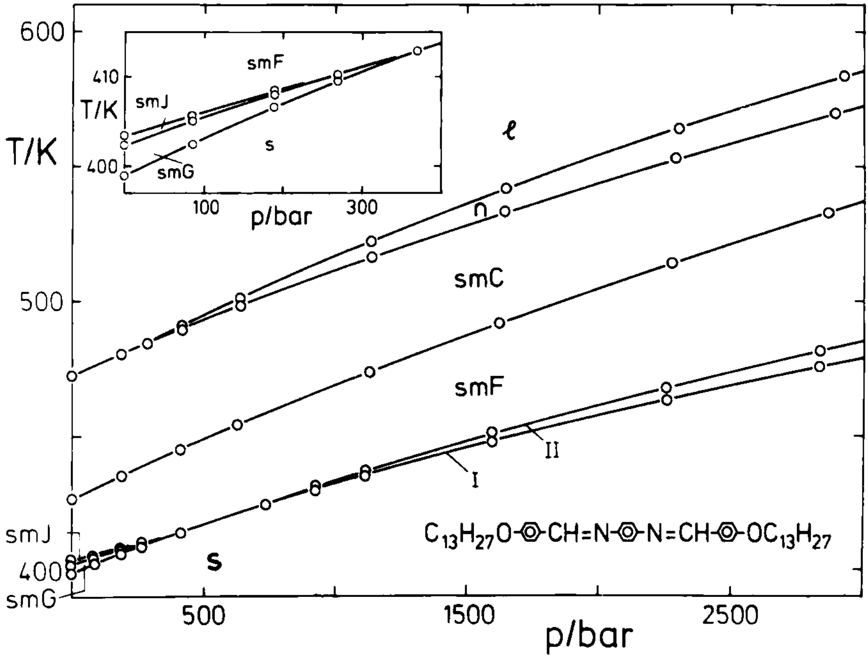

FIGURE 3 *T-p* phase diagram of bis-(4,4′-*n*-tridecoxybenzylidene)-1,4-phenylenediamine (TRIDOBPD)

members of the homologous series with shorter alkoxy chains exhibit the nematic phase at atmospheric pressure and that for these compounds the nematic phase is stabilized with increasing pressure. This is the first observation of a pressure induced nematic phase following a smectic *C* phase. A pressure induced nematic phase in a pure smectic *A* compound has already been identified microscopically by Cladis *et al.*[11]

The *T-p* phase diagram of TETDOBPD (Figure 4) is characterized by the same types of triple points as TRIDOBPD. Again the nematic phase is pressure induced at a triple point *smC*/*n*/*l* at about 680 bar and 497K. The *smJ* and *smG* phases vanish at triple points *smG*/*smJ*/*smF* at about 185 bar and 404 K and *s*/*smG*/*smF* at about 245 bar and 406 K, respectively. The temperature range of the *smF* phase is 25 K at 1 bar and 51 K at 3 kbar. At pressures higher than 915 bar and temperatures above 426 K the transitions I and II were found again.

The simplest of the four *T-p* phase diagrams presented is that of BOBPD (Figure 5). At atmospheric pressure only the nematic liquid crystalline phase has been observed, with a remarkable wide temperature range of about 108 K which is drastically increased with increasing pressure. The *s*3 phase vanishes at a triple point *s*2/*s*3/*n* at about 60 bar and 459.4 K.

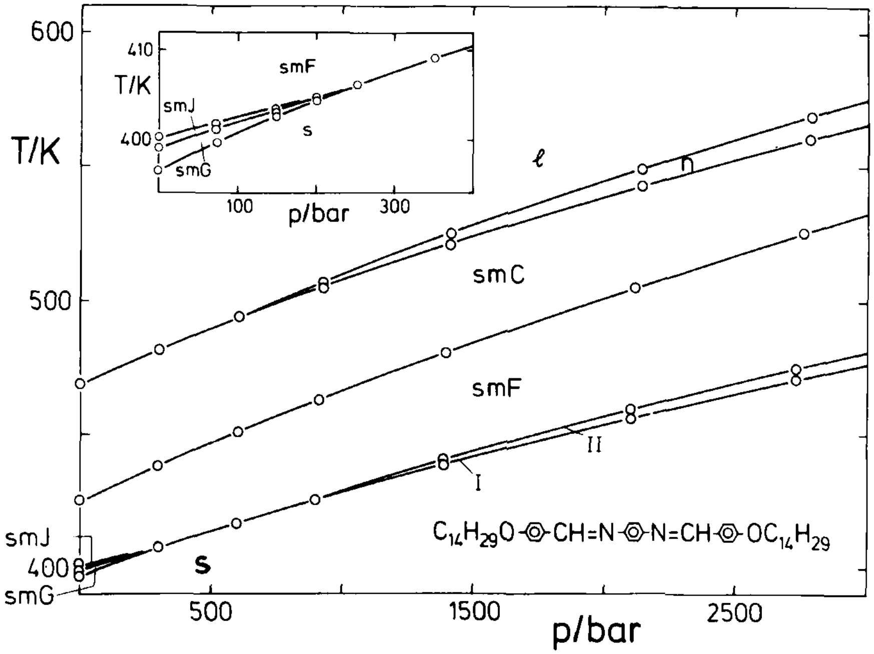

FIGURE 4 *T-p* phase diagram of bis-(4,4′-*n*-tetradecoxybenzylidene)-1,4-phenylenediamine (TETDOBPD)

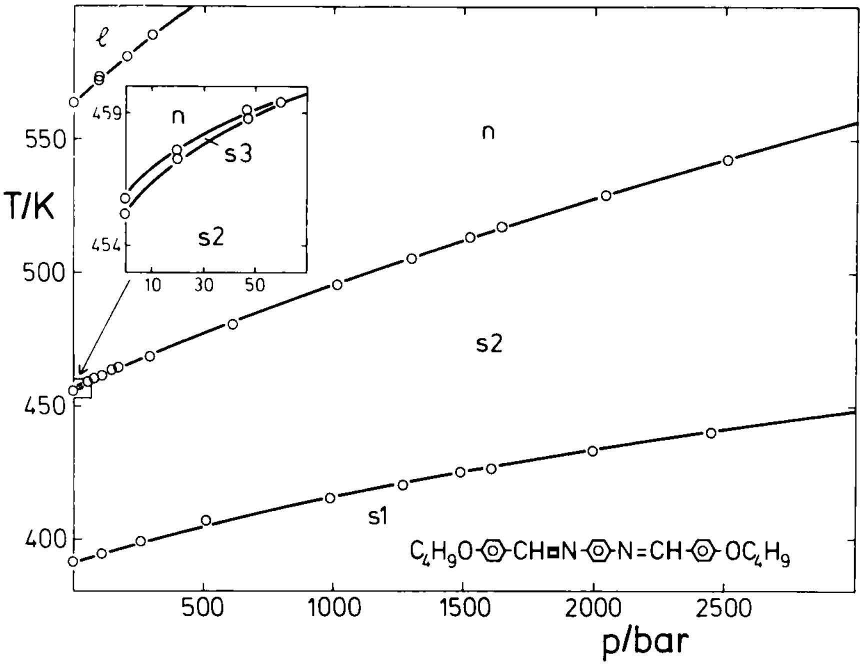

FIGURE 5 *T-p* phase diagram of bis-(4,4′-*n*-butoxybenzylidene)-1,4-phenylenediamine (BOBPD)

CONCLUSIONS

Figures 2–5 show that all transition temperatures are shifted to higher temperatures with increasing pressure where, however, considerable differences concerning the stability range of the different mesomorphic phases are observed. These effects suggest that pressure has an important influence on the ordering of the phases.

The nematic phase is obviously stabilized or even induced by pressure. This is demonstrated by the existence of a pressure induced nematic phase in TRIDOBPD and TETDOBPD, and by the increase of the temperature range of the nematic phase with increasing pressure for the homologues with shorter alkoxy chains. The latter effect is the less pronounced the longer the alkoxy chains are. These phenomena might be explained by the pressure induced increase of density that makes the molecular long axes more parallel and brings them closer together. Thus the molecules are hindered to slide as easily along each other as before.[10] As a consequence the nematic order might be favorised in comparison with the isotropic liquid and a pressure induced nematic phase appears or at least the nematic phase is stabilized.

The behaviour of smectic phases is more complicated. Here the stability range of the *smG* and the *smJ* phases, respectively, decreases and the phases even vanish at higher pressures. The same effect holds for the *smC* phase and it might be deduced from the experiments that the *smC* phase will also vanish at much higher pressures. The stability range of the *smF* phase, however, is extended.

The behaviour of low temperature smectic phases under pressure (e.g. *smG*) might be explained from a weakening of the interlayer forces in these highly ordered phases. This weakening could be produced by molecular movements to minimize the volume. The molecules and the layers would then be forced to change their positions with respect to each other thus disturbing the structure of these phases. This hypothesis has to be reconsidered with respect to the *smJ* phase, the structure of this new smectic phase being still unknown (for the structure of the *smG* phase see e.g. reference 12).

Since the molecules have a greater degree of freedom within the high temperature smectic phases, the interlayer forces and the order within the layers seem to be less important than for the low temperature smectics. Thus the high temperature smectic phases might be able to compensate the pressure influence by molecular movements which would already destroy the order and thus the stability of the low temperature smectics.

In conclusion pressure increase seems to reduce the stability range of low temperature smectic phases by destabilizing the structure of these highly ordered phases. High temperature smectic phases, however, seem to be able to overcome this influence and they can even be stabilized with increasing pressure.

Acknowledgment

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