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

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To cite this article: W. Spratte & G. M. Schneider (1979): Smectic Polymorphism of Some Bis-(4,4′-n-alkoxybenzylidene) - 1,4-phenylenediamines up to 3 kbars by Differential Thermal Analysis, Molecular Crystals and Liquid Crystals, 51:1-2, 101-115

To link to this article: http://dx.doi.org/10.1080/00268947908084696

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 101–116
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Printed in Holland

Smectic Polymorphism of Some Bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamines up to 3 kbars by Differential Thermal Analysis

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(*Received May 25, 1978; in final form August 31, 1978*)

The T-p phase diagrams of four homologues of the bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamine series ($C_5H_{11}O$ = PENTOBPD, $C_6H_{13}O$ = HEXOBPD, $C_7H_{15}O$ = HEPTOBPD and $C_8H_{17}O$ = OOBPD) have been determined by high pressure differential thermal analysis (dta) up to 3 kbars and in the temperature range 300 K to 600 K.

In each substance at least two solid phases are found at atmospheric pressure. HEPTOBPD and OOBPD exhibit five and HEXOBPD four smectic phases when heated from the solid up to the nematic state at normal pressure whereas PENTOBPD only exhibits the nematic phase. The rather complex phase behaviour of HEXOBPD, HEPTOBPD, and OOBPD gets simpler as pressure is increased. For each of the three compounds two smectic phases disappear in the pressure range of the experiments. Triple points between three smectic phases have been found in OOBPD, HEPTOBPD, and HEXOBPD; they are supposed to be the first examples for triple points involving mesomorphic phases only.

From the areas of the dta peaks the transition enthalpies were determined up to 2.4 kbars. By means of these values and the slopes of the T-p transition curves at different pressures the transition volumes could be additionally calculated.

A phase theoretical analysis of the results demonstrates that for this homologous series pressure increase has a similar influence on the T-p phase diagrams as it would have a shortening of the alkoxy chains at a constant (e.g. normal) pressure; a similar effect has been found for the transition enthalpies.

INTRODUCTION

During the last few years several papers have been published concerning the phase behaviour of liquid crystals under high pressure. Most of them mainly describe the behaviour of nematic and cholesteric phases under pressure,[1–3,30,31] others the so-called tricritical points on the T-p transition lines of the smA/cholesteric transition.[2,4–7] Pressure induced mesomorphism has been found for the first time by Shashidhar, *et al.*[8,9] in 4-methoxy- and 4-ethoxybenzoic acid. PVT data have been given by several authors during the last two years.[10–12] All these papers, however, do not systematically treat the pressure behaviour of smectic phases whereas investigations of smectic polymorphism at atmospheric pressure are numerous; here the changes in structure between the differently ordered smectic phases (smE, smG, smH, smB and others) are intensively discussed e.g. with respect to the position of the molecules or the tilt angles in the layers.[13–16]

Additional high pressure investigations were supposed to improve the knowledge and the understanding of smectic polymorphism. For the own experiments differential thermal analysis (dta) was used since thermal methods such as dta and dsc were found to be more informative for the high pressure investigation of smectic phases than e.g. visual observation or even polarization microscopy where transitions between smectic as well as solid phases are often difficult to be detected. Additionally from dta experiments a rather comprehensive thermodynamic description of the phase behaviour of liquid crystals can be deduced, even at high pressure.

For the experiments four members of the homologous series bis-(4,4′-*n*-alkoxybenzylidene)-1,4-phenylenediamine have been used: the octoxy (OOBPD), the heptoxy (HEPTOBPD), the hexoxy (HEXOBPD), and the pentoxy (PENTOBPD) compounds, respectively. These substances have been chosen because, except for PENTOBPD, they exhibit at least four smectic phases at atmospheric pressure and hence results for different smectic phases can be obtained in a single experimental dta run (Figures 2 and 3).

EXPERIMENTAL

a. Apparatus

Details of the experimental set up are described elsewhere.[17,18,20] For the measurements of the present work, however, a new high pressure dta autoclave has been constructed that is shown in Figure 1. In this autoclave the thermocouple junctions are soldered into two blind plugs which are then screwed from below into the pressure vessel; a similar principle has been used by Würflinger[19] for high pressure dta at low temperatures.

b. Experimental procedure

The experimental procedure (e.g. determination of transition temperatures, typical sample sizes) is treated elsewhere.[1] In the following some essential changes are summarized: For the high pressure measurements lead instead

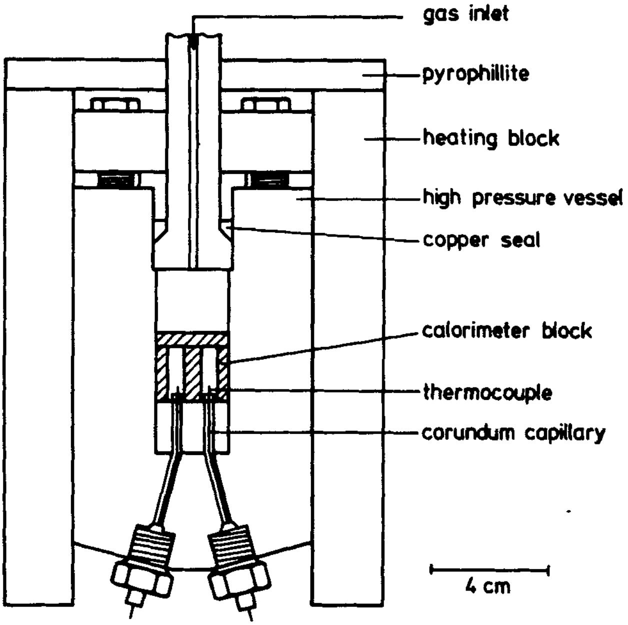

FIGURE 1 High pressure vessel see Ref. 20).

of indium capsules have been used because of the high temperatures normally involved. Most of the measurements were performed at a heating rate of 2 K. min^{-1}; at atmospheric pressure and near triple points the heating rate was 1 K. min^{-1}. The enthalpy calibration at atmospheric pressure was carried out with bis-4,4′-*n*-heptoxyazoxybenzene using the melting enthalpy given by Arnold.[21] The determination of transition enthalpies at elevated pressures is more difficult since all peak areas decrease with rising pressure because of the increasing heat conductivity of the pressurizing gas. This effect has been ruled out by comparing the changes of peak areas of hexacosane and the liquid crystal EBBA at high pressure with those of the substances under test. The high pressure values of the transition enthalpies of hexacosane[22] and EBBA[23] have been determined by high pressure dsc. All experiments, including calibrations with hexacosane and EBBA, were done under the same conditions with respect to material of capsules, heating rates etc. For details of the calibration procedure for the determination of enthalpies at atmospheric and elevated pressures see Ref. 20.

c. Substances

OOBPD was purchased from the Eastman Kodak Company. PENTOBPD, HEXOBPD, and HEPTOBPD were synthesized from the corresponding

4-*n*-alkoxybenzaldehyde and 1,4-phenylenediamine in absolute ethanol using acetic acid as catalyst. The four substances were recrystallized several times from benzene and ethanol until no changes in the nematic/liquid isotropic transition temperatures were observed. No substantial amount of impurities was found by thin layer chromatography.

d. Accuracy

The accuracy of the temperature measurement was better than ±0.5 K up to 500 K and better than ± 1 K above this temperature. Since according to earlier experiments[32] pressure is transduced to the samples through the thin walls of the lead cells without hysteresis, cell and line pressures are the same within the limits of experimental error (±5 bars). For transition enthalpies above 2 kJ.mole^{-1} the accuracy of the enthalpies is ±5% at atmospheric

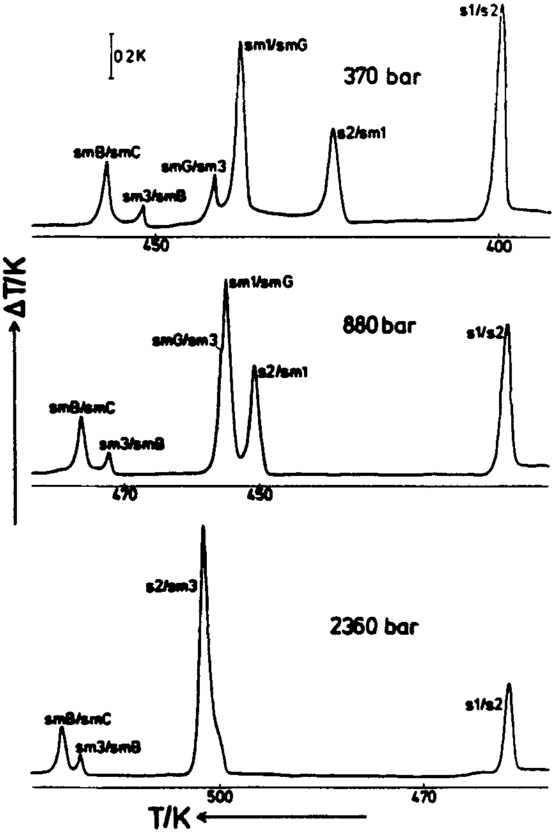

FIGURE 2 Original dta traces of HEPTOBPD at different pressures.

pressure and ± 15% at elevated pressures and that of the transition volumes ± 10% and ± 20% respectively; for smaller ΔH-values the corresponding accuracies of the enthalpies are ± 10% and ± 20% and that of the transition volumes ± 15% and ± 25%, respectively.

RESULTS

The symbols used throughout the present work to designate the phases present are the following: s for the solid, sm for the smectic, n for the nematic and l for the liquid isotropic phases. Different solid and smectic phases are distinguished by numbers and capital letters; the latter are used for the smectic phases as far as their structures are known up to now.[24]

Six characteristic dta traces obtained experimentally are represented in Figures 2 and 3 for OOBPD and HEPTOBPD at different pressures; the

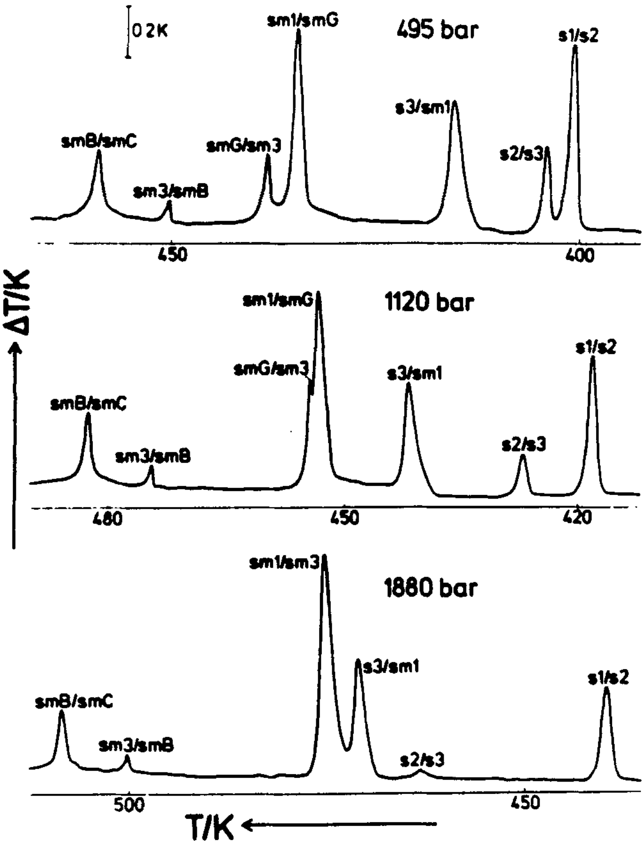

FIGURE 3 Original dta traces of OOBPD at different pressures.

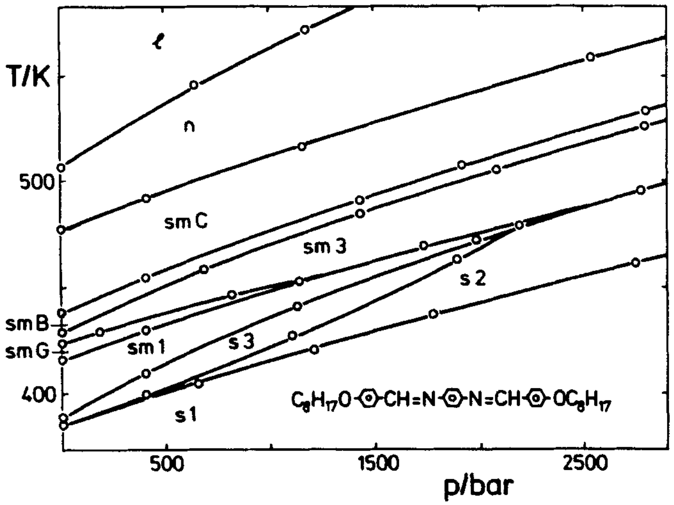

FIGURE 4 T-p phase diagram of OOBPD.

smC/n and n/l transitions are omitted in these figures. From about 50 dta traces at different pressures for each substance the transition temperatures were determined and selected values are plotted versus pressure in Figures 4 to 7. From the T-p phase diagrams the data compiled in Tables I to IV were obtained by interpolation. In these tables the transition enthalpies as a function of pressure are also summarised. For the calculation of the transition volumes from the Clapeyron equation the slopes of the transition curves at

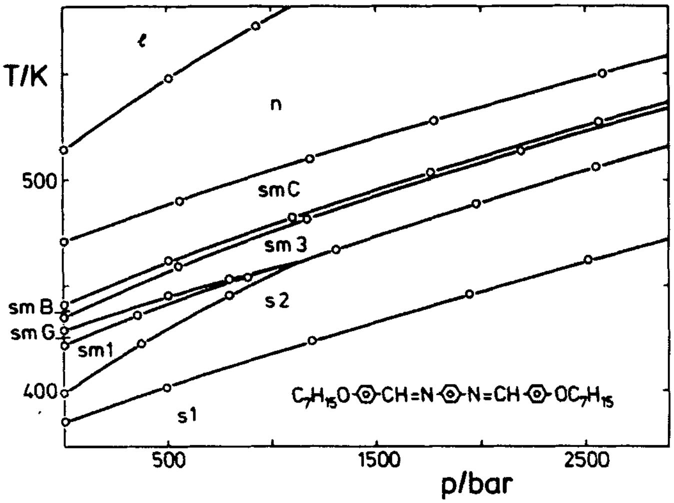

FIGURE 5 T-p phase diagram of HEPTOBPD.

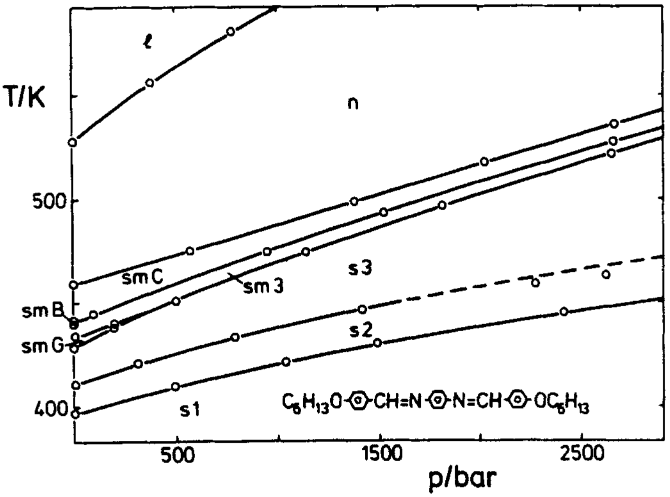

FIGURE 6 T-p phase diagram of HEXOBPD.

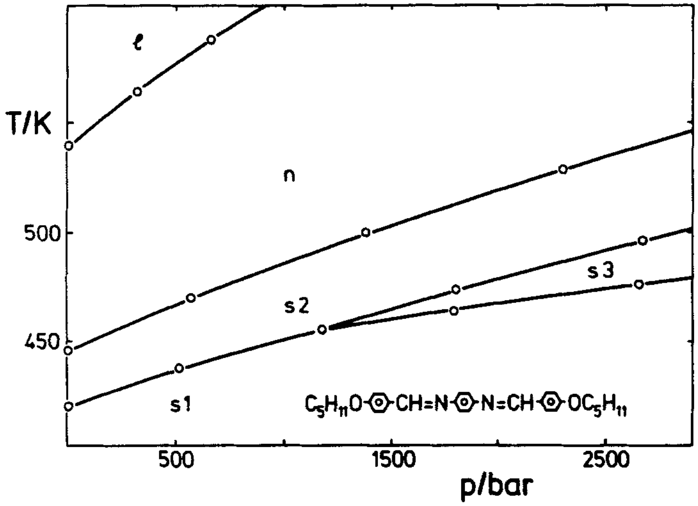

FIGURE 7 T-p phase diagram of PENTOBPD.

different pressures are necessary. These are obtained by least-square fitting of the experimental T-p values to polynomials in p of the type $T = a + bp + cp^2$. The calculated ΔV values at different pressures along the coexistence lines are also given in Tables I to IV.

DISCUSSION

The phase transition temperatures determined in this work at atmospheric pressures are in good agreement with those reported by Arora *et al.*[25] Additionally one solid/solid transition for OOBPD, HEPTOBPD, and PENTOBPD and two solid/solid transitions for HEXOBPD have been

TABLE I

Transition temperatures T, transition enthalpies ΔH, and transition volumes ΔV of OOBPD as a function of pressure along the coexistence lines

p/bar	s1/s2	s2/s3	s3/sm1	sm1/smG	smG/sm3	sm3/smB	smB/smC	smC/n	n/1
T/K									
1	385.0[a]		389.0	416.2	423.5	428.6	438.0	477.4	506.2
400	396.9	399.2	409.3	429.2	435.4	445.9	454.3	491.4	530.5
800	408.8	415.0	427.3	441.7	445.6	461.9	469.1	505.0	552.5
1200	420.3	431.4	443.5	453.8	454.9	476.2	483.2	517.9	572.5
1600	431.5	449.4	458.1	465.0[b]		489.6	496.5	530.3	591.0
2000	442.4	469.3	471.7	475.0[b]		502.2	509.3	542.4	
2400	452.9	484.9[d]				514.3	521.3	554.3	
2800	462.8	495.7[d]				525.7	533.2	565.7	
ΔH/kJ.mol^{-1}									
1	10.2[a]		6.7	5.3	1.4	0.36	2.3	2.8	1.4
400	6.7	3.2	7.0	7.2	1.5	0.43	3.1	3.2	1.7
800	7.0	2.6	7.6	9.0	1.7	0.50	3.4	3.4	1.9
1200	7.3	2.1	8.2	15.4[b]		0.56	3.7	3.5	2.0
1600	7.7	1.5	8.7	18.3[b]		0.64	3.9	3.6	2.1
2000	8.0	0.7	31.5[c]			0.70	4.1	3.7	
2400	8.3	35.1[d]							
ΔV/cm^{3}mol^{-1}									
1	8.2[a]		9.2	4.3	1.0	0.37	2.2	2.1	1.8
400	5.1	3.0	8.3	5.5	1.0	0.40	2.7	2.2	1.9
800	5.1	2.6	7.9	6.4	1.0	0.42	2.7	2.2	1.8
1200	5.0	2.2	7.3	9.0[b]		0.43	2.7	2.2	1.7
1600	5.0	1.6	6.7	10.2[b]		0.44	2.6	2.1	1.6
2000	4.9	0.8	18.8[c]			0.44	2.6	2.1	
2400	4.8	21.3[d]							

[a] s1/s3; [b] sm1/sm3; [c] s3/sm3; [d] s2/sm3.

found in the present work. The solid/solid transitions have also been detected by Garn.[26] In his measurements on OOBPD, HEPTOBPD, and HEXOBPD up to ten bars[27] the transition temperatures are too low by more than 10 K in some cases. Here the substances under test were not separated from the pressure transmitting gas normally resulting in a depression of the transition temperatures. Besides the temperature increase found by Garn is too large for a pressure increase of 10 bars only.

Our investigations at atmospheric pressure confirm the statement of Arora[25] that the so-called sm1 phases of OOBPD and HEPTOBPD are smectic and not solid phases such as proposed by Demus and Rurainski.[28] This is verified by polarization microscopy[20] and by the absence of any supercooling for the smG/sm1 transition. Up to now the sm1 and sm3 phases are not yet identified; they are probably tilted phases (see Conclusions).

TABLE II

Transition temperatures T, transition enthalpies ΔH, and transition volumes ΔV of HEPTOBPD as a function of pressure along the coexistence lines

p/bar	s1/s2	s2/sm1	sm1/smG	smG/sm3	sm3/smB	smB/smC	smC/n	n/l
				T/K				
1	385.0	398.4	421.7	428.9	434.7	441.2	471.0	513.4
400	397.5	423.5	437.2	441.7	452.4	457.0	484.7	540.4
800	410.2	445.3	451.2	453.2	468.4	472.2	497.7	565.3
1200	422.9		463.5^b		482.5	485.8	510.4	
1600	435.5		476.8^b		495.6	498.5	522.3	
2000	447.4		489.4^b		508.0	510.9	534.0	
2400	459.1		501.4^b		519.8	522.6	545.2	
				ΔH/kJ.mol^{-1}				
1	12.7	5.2	6.8	1.5	3.2^c		2.7	1.1
400	11.9	6.2	12.3^a		4.1^c		3.0	1.4
800	11.4	7.3	14.7^a		4.9^c		3.2	1.6
1200	11.0		26.5^b		5.7^c		3.5	
1600	10.6		30.1^b		6.5^c		3.8	
2000	10.3		33.7^b		7.3^c		4.0	
2400	9.9		37.3^b		8.1^c		4.3	
				ΔV/cm^{3}mol^{-1}				
1	11.0	9.0	6.7	1.2	3.0^c		2.0	1.6
400	9.8	8.8	9.6^a		3.5^c		2.1	1.7
800	9.0	8.3	10.0^a		3.8^c		2.1	1.7
1200	8.2		19.7^b		4.0^c		2.2	
1600	7.6		20.8^b		4.2^c		2.2	
2000	7.0		21.7^b		4.3^c		2.2	
2400	6.4		22.4^b		4.4^c		2.2	

[a] sm1/sm3; [b] s2/sm3; [c] sm3/smC.

For the smB phase the old nomenclature of Demus is still used; at present for tilted smectic phases the sequence smC/smF/smH/smG is discussed in the literature.[33]

In the following some additional informations will be given for the substances measured. For details see Ref. 20.

a. OOBPD

The T-p phase diagram in Figure 4 is characterized by four triple points: s1/s2/s3 (386 K; 50 bars), s2/s3/sm1 (475 K; 2110 bars), s2/sm1/sm3 (484 K; 2390 bars), and sm1/sm3/smG (457 K; 1320 bars), the accuracy of these and all following triple point data being about ± 1 K and ± 30 bars, respectively.

TABLE III

Transition temperatures T, transition enthalpies ΔH, and transition volumes ΔV of HEXOBPD as a function of pressure along the coexistence lines

p/bar	s1/s2	s2/s3	s3/smG	smG/sm3	sm3/smB	smB/smC	smC/n	n/I
				T/K				
1	396.7	411.0	428.2	433.2	440.2	441.0	459.0	527.5
400	407.1	422.7	447.0^{b}		455.6^{a}		470.4	556.7
800	416.4	433.0	462.2^{b}		469.7^{a}		482.0	580.7
1200	424.5	441.9	476.2^{b}		483.0^{a}		493.5	
1600	432.0	450.2	489.4^{b}		495.7^{a}		504.9	
2000	438.8		502.0^{b}		508.0^{a}		516.4	
2400			514.3^{b}		519.9^{a}		527.9	
2800			526.1^{b}		531.4^{a}		539.4	
				ΔH/kJ.mol^{-1}				
1	8.8	3.5	19.0^{b}		4.6^{a}		2.3	1.3
400	9.1	3.7	22.0^{b}		5.3^{a}		2.6	1.5
800	9.6	3.9	25.0^{b}		6.0^{a}		3.0	1.7
1200	10.1	4.2	28.0^{b}		6.7^{a}		3.3	
1600	10.5	4.4	31.0^{b}		7.5^{a}		3.6	
2000			34.0^{b}		8.3^{a}		3.9	
				ΔV/cm^{3}mol^{-1}				
1	6.0	2.6	19.9^{b}		4.0^{a}		1.5	1.9
400	5.5	2.4	18.5^{b}		4.2^{a}		1.6	1.8
800	5.1	2.2	19.8^{b}		4.5^{a}		1.8	1.7
1200	4.8	2.0	20.6^{b}		4.7^{a}		1.9	
1600	4.6	1.8	21.1^{b}		4.9^{a}		2.1	
2000			21.6^{b}		5.0^{a}		2.2	

[a] sm3/smC; [b] s3/sm3.

The sm1/sm3/smG triple point is supposed to be the first that has been found between mesomorphic phases only.

The s2/s3 transition is interesting from several aspects. It only exists between 50 bars and 2110 bars and the slope of the T-p coexistence curve increases with increasing pressure in contrast to the decrease of the slope normally found. The transition enthalpy and the volume change which are about 4 kJ.mol^{-1} and 3.5 cm^{3}mol^{-1} at 50 bars approach nearly zero at the s2/s3/sm1 triple point (see Table I and Figure 3). The scattering of the measuring points (±3 K) and the broadening of the peaks near this triple point becomes rather significant. These findings suggest that the s2 and s3 phases become nearly identical at the triple point, an effect that resembles critical behaviour.

TABLE IV

Transition temperatures T, transition enthalpies ΔH, and transition volumes ΔV of PENTOBPD as a function of pressure along the coexistence lines

p/bar	s1/s3	s3/s2	s2/n	n/1
T/K				
1	421.3[a]		446.5	539.0
400	434.4[a]		463.5	570.0
800	446.2[a]		479.0	596.0
1200	456.3[a]		493.2	
1600	461.5	468.1	506.3	
2000	467.2	479.0	519.8	
2400	473.0	489.5	532.1	
ΔH/kJ.mol^{-1}				
1	4.8[a]		26.0	1.1
400	5.2[a]		29.5	1.3
800	5.6[a]		33.1	1.5
1200	6.0[a]		36.7	
1600	2.6	3.8	40.3	
2000	2.9	4.0	43.9	
2400	3.2	4.2	47.5	
ΔV/cm^{3}mol^{-1}				
1	4.1[a]		24.6	1.7
400	3.8[a]		25.6	1.6
800	3.5[a]		26.4	1.5
1200	3.2[a]		26.9	
1600	0.8	2.3	27.2	
2000	0.9	2.3	27.1	
2400	1.0	2.3	26.9	

[a] s1/s2.

From Table I another interesting effect can be deduced. The sum of the transition enthalpies sm1/smG and smG/sm3 at 1800 bars is three times as large as 1 at bar; a similar effect is demonstrated by the pressure dependence of the ΔV values. This can be explained by a strong effect of pressure on the sm1 phase. Evidently this phase resembles more and more a solid one. This is also affirmed by the supercooling (up to about 4 K) of the phase transitions smG/sm1 and sm3/sm1 at high pressures and by the fact that the sm1/sm3 transition has by far the highest transition enthalpy at 1800 bars.

b. HEPTOBPD

The phase diagram of HEPTOBPD in Figure 5 is essentially the same as that of OOBPD, except for the absence of the s2/s3 transition. The triple points s2/sm1/sm3 (462 K; 1140 bars) and sm1/sm3/smG (461 K; 1120 bars) are very close together and shifted to lower pressures in comparison with OOBPD. Thus here again a triple point involving mesomorphic phases only is found.

From Table II and Figure 2 it can be deduced that the increase of the sum of the transition enthalpies sm1/smG and smG/sm3 with pressure is very large; the effect, however, is not so marked as for OOBPD. The same is true for the ΔV values. The reason seems to be the same as for OOBPD: The sm1 phase slowly turns over to a solid-like one which is again demonstrated by an increasing supercooling effect of the smG/sm1 and sm3/sm1 transitions with rising pressure.

c. HEXOBPD

The phase diagram of HEXOBPD is given in Figure 6. This substance exhibits two triple points: s3/smG/sm3 (443 K; 300 bars) and sm3/smB/smC (442 K; 50 bars) the latter again involving smectic phases only. The range for the smB phase is rather small. The sm1 phase has vanished in comparison with OOBPD and HEPTOBPD. The solid phase s3 is identified by polarization microscopy,[20] by the fact that the transitions smG/s3 and sm3/s3 are supercooling by about 5 K and, most important, by the high value of the s3/sm3 transition enthalpy even at 1 bar (19 kJ.mol^{-1}). The increase of this enthalpy change with increasing pressure is not so important and the volume change remains constant within experimental error. The transition temperatures and enthalpies of the two solid/solid transitions s1/s2 and s2/s3 can be determined with high accuracy and reproducibility up to about 1500 bars. Above this pressure the sharp peaks change into broader ones and the transition temperatures, especially for the s2/s3 transition (see Figure 6), are depressed by sometimes more than 5 K. This may be explained from the assumption that on cooling the solid/solid phase transformation is hindered and that on following heating the resulting mixture of s2 and s3 melts some degrees lower than pure solid 2.

d. PENTOBPD

The phase diagram of PENTOBPD in Figure 7 is the simplest of all. Two solid phases s1 and s2 are observed at atmospheric pressure. Another solid phase s3 appears above the s1/s2/s3 triple point (456 K; 1200 bars). The s2/n transition enthalpy is the largest of all and the volume change is nearly independent of pressure.

CONCLUSIONS

Increase of pressure brings about an increase of all transition temperatures in the four compounds, but there is an obvious difference concerning the stability of the liquid crystalline phases.

For all substances under test an increase of the nematic range is found at high pressures. This is the normal behavior of nematic states under pressure. Since here pressure increase mainly causes a decrease of the intermolecular distances, the van der Waals interactions are getting more important and so the nematic range is extended.[23] The initial slopes of the T-p curves for the nematic/liquid isotropic transitions are much greater than the slopes of the other curves (except for the s2/sm1 transition in HEPTOBPD). The shorter the alkoxy chains the larger are the initial slopes of the clearing curves e.g. OOBPD has a slope of 62.9 $K.kbar^{-1}$, HEPTOBPD 70.9 $K.kbar^{-1}$, HEXOBPD 77.9 $K.kbar^{-1}$, and PENTOBPD 83.5 $K.kbar^{-1}$.

In general the overall smectic range of HEXOBPD, HEPTOBPD, and OOBPD is reduced with increasing pressure, for the first compound one may even expect the smectic range to disappear completely at very high pressures. A shrinkage of the sm1, smG, smB, and smC phase ranges with increasing pressure has been found experimentally; for the sm1 and smG phases this shrinkage is so strong that they disappear completely up to 3 kbars. The sm3 phase of OOBPD and HEPTOBPD is the only one for which an enlargement of the smectic range with rising pressure is observed whereas the range of the corresponding phase in HEXOBPD remains nearly constant.

From the T-p phase diagrams in Figures 4 to 7 it can be roughly estimated that pressure increase influences the phase behavior in the same way as shortening of the alkoxy chains does, e.g. a similar phase behavior as for HEXOBPD at low pressure can be obtained in the high pressure range of HEPTOBPD.

Three facts support this hypothesis:

1) The pressure range of the sm1 phase becomes smaller going from OOBPD to HEXOBPD. The sm1 phase is limited to pressures below 2400 bars in OOBPD, to below 1100 bars in HEPTOBPD and in HEXOBPD this smectic phase has already completely vanished.

2) The considerable increase of the transition enthalpy along the sm1/smG and the sm1/sm3 coexistence lines for HEPTOBPD and OOBPD, respectively, corresponds to a large s3/smG transition enthalpy in HEXOBPD already at atmospheric pressure.

3) At high pressures the nematic range is increased and the smC as well as the total smectic range is decreased in OOBPD, HEPTOBPD, and HEXOBPD. A similar phase behavior can be achieved by shortening of the alkoxy chains at 1 bar.

According to X-ray and dilatometric measurements of Guillon and Skoulios[29] at normal pressure on the homologous series bis-4,4′(*n*-alkoxybenzylideneamino)biphenyl, that only differs from the substances of the present work by one additional phenylene group and that exhibits a very similar phase behavior, the molecules of all smectic phases are tilted in the layers, the tilt angle becoming greater with increasing chain length. Similar tilting angles will probably exist for the substances under test. The pressure effect described above can be qualitatively understood from the assumption that increasing pressure and consequently increasing density will force the molecules to raise in the layers accompanied by a decrease of the tilt angles. This effect is the more pronounced the longer the alkoxy chains are. It is most significant for the sm1 phase as it is seen in Table I and II and in Figures 4 and 5.

From the results it might be deduced that the stability range of "tilted smectic phases" generally decreases with increasing pressure. In order to get more experimental informations the investigations are continued with other members of the same homologous series.

Acknowledgments

Financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie e.V. is gratefully acknowledged.

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