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Two Liquid Crystal Phases with Nematic Morphology in Laterally Substituted Phenylenediamine Derivatives‡

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Abstract—Bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines and bis-(4′-*n*-alkoxybenzal)-2-methyl-1,4-phenylenediamines with different alkoxy groups have been synthesized. Similar compounds with fluoro, bromo and chloro groups replacing the alkoxy groups have also been prepared. All the compounds show a nematic liquid phase.

An additional lower temperature liquid crystalline phase is observed with chloro-substituted compounds for *n*-alkoxy chain lengths of C_8 and longer and with the methyl substituted compounds for chain lengths of C_{10} and longer. This lower temperature phase can show a threaded texture very similar to the nematic phase. Furthermore, both phases can be uniformly oriented by surface action and can assume a twisted structure. We suppose that the lower temperature phase has a layered structure in which the molecules are inclined to the layers, and that it corresponds to a smectic liquid crystal classified by Sackmann and Demus as smectic C.

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Introduction

We have found with some of bis-(4′-*n*-alkoxybenzal)-2-methyl-1,4-phenylenediamines and bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines two liquid crystalline phases, both of which have the optical morphology of nematic liquids. Similar observations have been made by Leclercq *et al.*,[1] with some other compounds. For the purposes of this discussion we will call the two phases nematic I and nematic II. By these terms we stress the apparent similarities between the two phases. The origin of the term " nematic " is based on the Greek word for threads and refers to optical features as described by Friedel.[2]

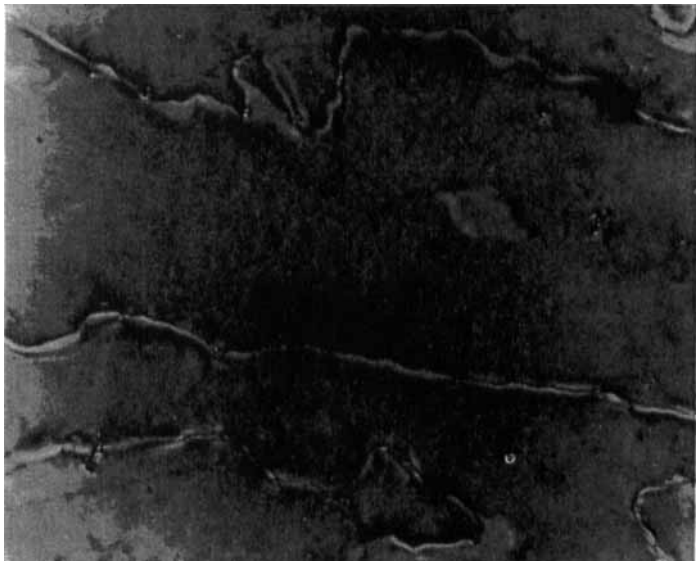
Some bis-(4′-*n*-alkoxybenzal)-1,4-phenylenediamines have also been prepared and we found several new smectic phases. The optical studies on these compounds have not yet been concluded and we give for them only the results of thermal measurements.

Optical Studies on Laterally Substituted Phenylenediamine Derivatives

All of the derivatives which we have synthesized have been examined using a Leitz Panphot Polarizing Microscope in order to assign an initial classification and to verify the type of phase transition. All the derivatives showed, upon cooling from the isotropic phase, a nematic phase. It is recognizable as nematic by the formation of droplets at the transition point, by its typical textures, and by its relatively low viscosity. In the case of long chain alkoxy derivatives with a chain length of C_8 and longer for chloro compounds, and C_{10} and longer for methyl compounds, on further cooling an additional phase of higher viscosity is formed. The change in texture is often small, although during the transition itself a considerable disturbance occurs. Figure 1a–c demonstrate these facts for the C_{18} chloro compound. It is interesting to note that the " threads " are preserved during the phase transition and retain their shape and position (compare Fig. 1a and 1c). The compounds with shorter chain length usually show

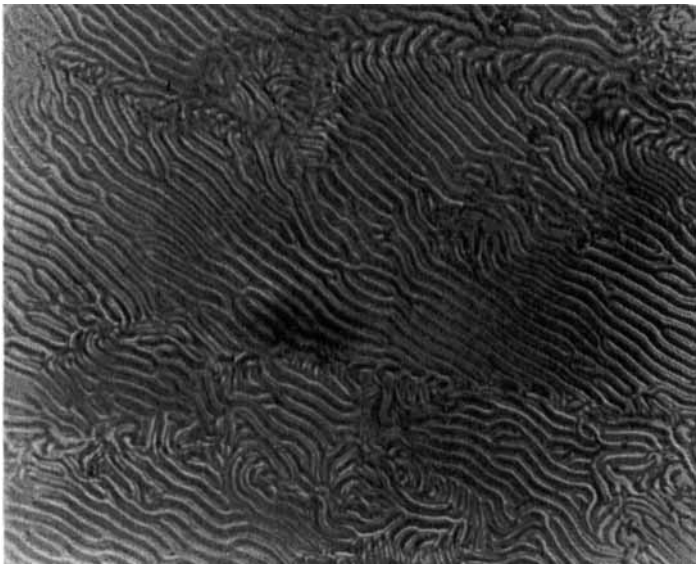
even a stronger similarity in their textures. Schlieren textures and marble textures as described by Sackmann and Demus[3] can be obtained in both phases.

Other similarities were observed with layers of bis-(4′-*n*-dodecyloxybenzal)-2-methyl-1,4-phenylenediamine between aligned surfaces. We rubbed glass slides as described by Zocher,[4] Chatelain[5] and others. Between glasses with parallel oriented directions of rubbing, upon cooling, well aligned nematic layers formed usually with a few threads. On cooling further, the alignment became somewhat less uniform which indicates a rearrangement of the molecules in approaching the second phase transition. At the transition point the alignment was lost temporarily and a texture formed like that shown in Fig. 1b. In nematic II a very

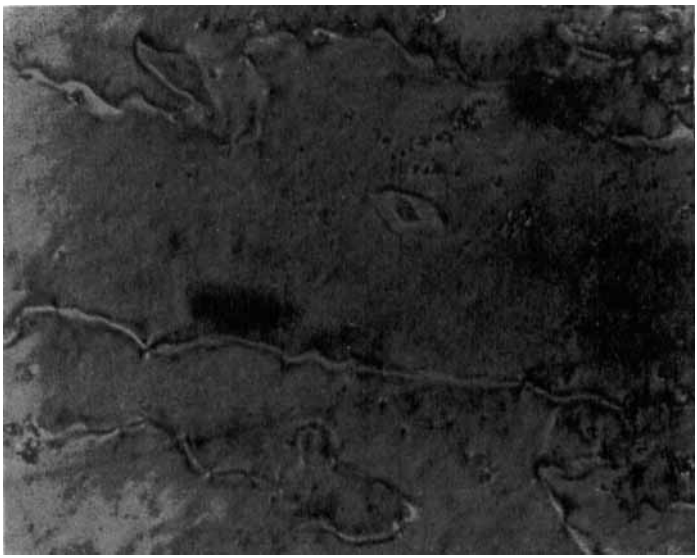


I(a)

Figure 1. Liquid crystalline states of Bis-(4′-*n*-octadecyloxybenzal)-2-chloro-1,4-phenylenediamine observed on cooling with crossed polarizers, magnification ~38. Sample thickness × 0.02 mm.
(a) Higher temperature liquid crystalline phase (nematic I).
(b) Transition between the two phases.
(c) Lower temperature phase (nematic II).



1(b)



1(c)

uniform alignment was recovered and the threads reappeared clearly. The direction of alignment was still determined by the direction of rubbing. Extinction was obtained in both phases between *crossed* polarizers, when the direction of polarization was parallel or perpendicular to the direction of rubbing. In these positions slight disturbances such as blowing on the coverslide caused strong light flashes in both phases.

Between glass slides with the direction of rubbing at right angles uniform but continuously twisted layers were formed. The continuous twist reveals itself by turning the direction of polarization of linear polarized light by an angle of 90°. In both phases extinction is obtained with these layers between *parallel* polarizers and the direction of polarization parallel or perpendicular to the direction of rubbing.

Observations on mixtures of bis-(4′-*n*-dodecyloxybenzal)-2-methyl-1,4-phenylenediamine and cholesteryl nonanoate were made using the procedure of Sackmann and Demus.[3] The unmixed substances were melted together between glass slides and gave a progression of concentrations in the contact region. For certain concentrations nematic II as well as nematic I showed colors due to optical activity which indicates that both liquids assume a spontaneously twisted structure.

In another test it was determined how the electric field affected the nematic II. A sample was prepared of the bis-(4′-*n*-dodecyloxybenzal)-2-methyl-1,4-phenylenediamine by placing it between two glass plates which were coated with tin oxide for conduction. The tin oxide was in contact with the liquid crystal. The estimated thickness of the sample was $\frac{1}{10}$ mm. Upon heating and allowing to cool into the nematic phase, the threaded texture was observed and upon application of a DC electric field, the number of threads began to increase at about 4 volts. As the field was increased, the number of threads increased. We continued to cool and no appreciable change was observed until the second phase transition. The threshold voltage at which the threads began to appear went from 4 volts to 15 volts in nematic II. The pattern was approximately the same as in nematic I. The

threshold voltage was still considerably lower than we had observed previously for a smectic phase.

Conclusions

Nematic II has some properties, as for instance the alignment by surfaces and the possibility of twisting, that previously have been regarded as unique properties of nematic liquids. But the following points indicate strongly that it really is a smectic phase:

1. It exists in a temperature range below a nematic phase.
2. The dependence of the transition temperatures (nematic II–nematic I) on chain length agrees with that generally found for smectic phases.
3. Besides a threaded Schlieren texture, a fanlike texture can also be observed.
4. Very recently we could observe focal conic textures in uncovered droplets which seem to be identical with those observable under the same conditions with some smectic liquids classified as smectic C (for instance with 4,4′-di-*n*-octyloxyazoxybenzene).

Characteristic for a smectic liquid is a layered molecular structure.‡ In addition to the parallel orientation of the molecules that are found in nematic liquids, the molecular centers are arranged in equidistant layers. A twisting with respect to the orientation of the molecular axis is compatible with this layer structure only if the *twist axis* at any point is normal to the layers. In smectic liquids classified as smectic A the molecules are oriented normal to the layers. These liquids have an infinite fold symmetry axis and cannot be twisted. But a twist without a disturbance of the layers becomes possible if the molecules are inclined against the layers. The twist can be realized by a gradual turning of the tilt direction from layer to layer.

The assumption of a tilted layer structure for nematic II can explain also the observation of Schlieren textures.[6] The threads

‡ Preliminary results of X-ray studies on nematic II confirm its layered structure. A. de Vries and G. H. Brown private communication.

in thin " uniformly " oriented layers separate areas with 180° different tilt directions. Since the birefringence color of adjoining areas was equal, the inclination of the molecules against the surface was also equal. We assume therefore that the molecular layers in our sample were parallel to the surface. Accordingly no symmetry axis of the liquid should be normal to the surface since the molecules are inclined. Observations with convergent light on a sample of the C_{12} methyl compound confirmed this conclusion. There was no principal axis of the indicatrix normal to the layer. We could not determine the position of an optical axis because of too strong inclination. The tilt angle of the molecules seems to be larger than 30°.

A texture similar to a nematic Schlieren texture has been previously observed with some smectic liquids,[3] classified as smectic C or smectic B. It seems possible that nematic II and smectic C are the same phase. It would indicate that smectic C differs in its structure from smectic A by an inclination of the molecules. The properties that we observed are perhaps due to an unusually large tilt angle or to an unusual surface action that strongly favors an arrangement of the molecular layers parallel, or nearly parallel, to glass surfaces.

Thermal Measurements

The optical studies were paralleled with differential thermal measurements. Transition temperatures and transition energies were determined using a DuPont 900 DTA equipped with a disc for differential scanning calorimetry. The transitions with highest transition energy have been regarded as melting points (solid-liquid or solid-liquid crystal transition). These were also always the transitions that can most easily be supercooled, whereas supercooling towards liquid crystal states is negligible. The assignments of the transitions were confirmed and completed by optical studies. The error of the temperature measurements is estimated to be smaller than $\pm 2\,^{\circ}C$; the accuracy of the transition energies in Fig. 2 is estimated to be ± 0.06 kcal/mole for the

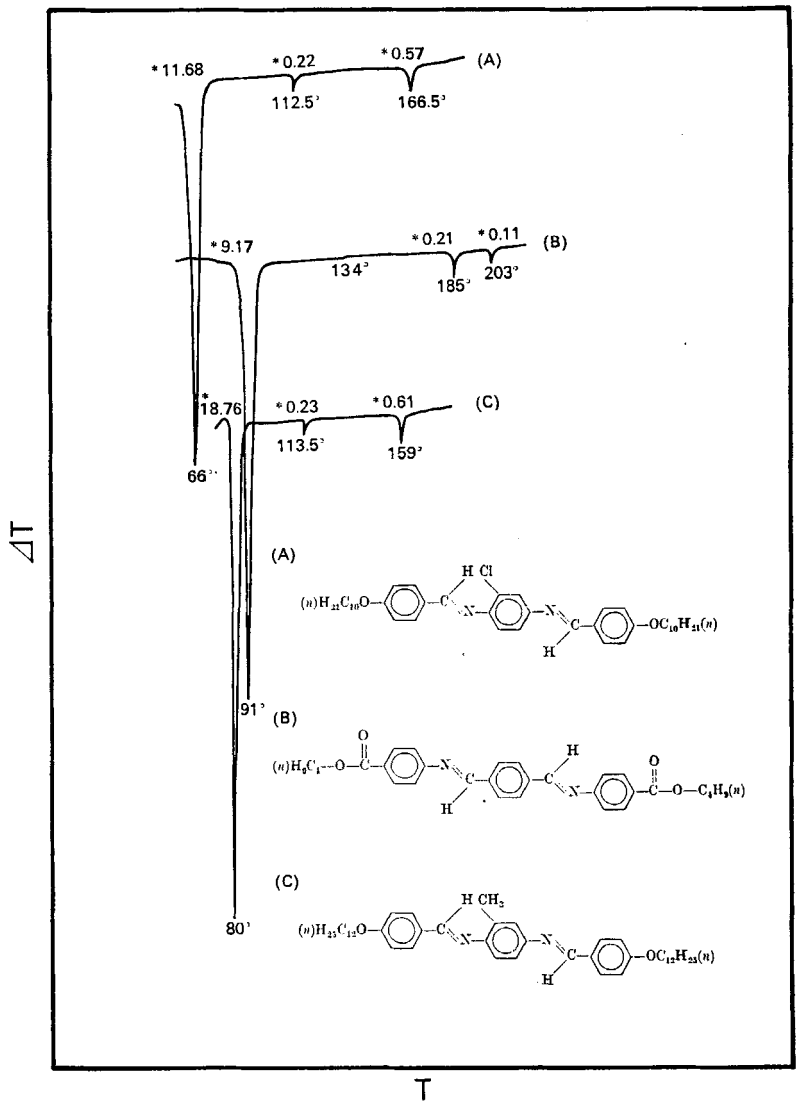


Figure 2. Differential thermograms of a terephthal derivative and two bis-(benzal)-phenylenediamine, heat of transitions marked with asterisks (in kcal/mole) and transition temperatures (in °C). The energy of the transition at 134 °C with compound (B) is very low and has not been determined.

transition with an energy of less than 0.3 kcal/mole, and below 15% for all other transitions. The transition energies found for nematic I to nematic II are comparable to those observed in many cases for the nematic to smectic transitions. A comparison of transition energies for some substances is given by Fig. 2. The energies for the isotropic-nematic transitions are relatively large for compounds (A) and (C), but Arnold[7] has also observed similar high transition energies for 4,4′-di-*n*-alkoxyazoxybenzenes with long alkyl chain substituents. Compound (B) has a nematic phase and two smectic phases, which we classified optically as smectic A and, at a lower temperature, probably smectic C.

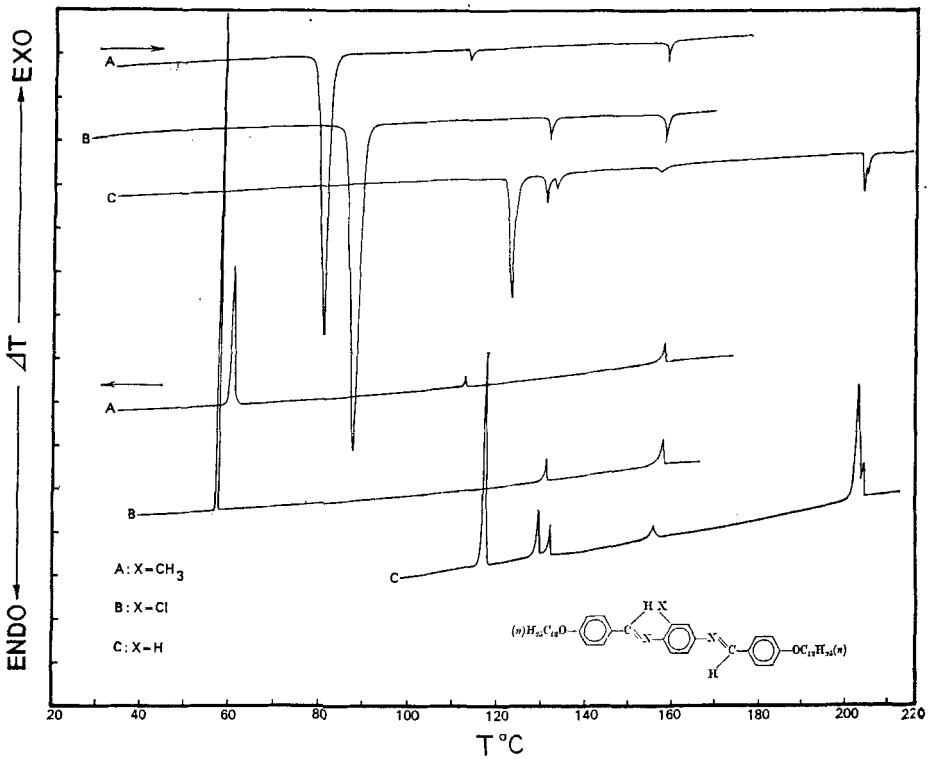
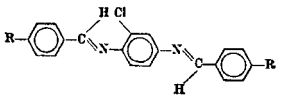


Figure 3. Differential thermograms of various bis-(4′-*n*-dodecyloxybenzal)-1,4-phenylenediamines. The cooling curve for (C) is at 2.5 times increased sensitivity.

In Fig. 3 we have compared the phase transitions of the dodecyloxy derivatives of laterally substituted series with the phase transition of the non-laterally substituted dodecyloxy derivative. The non-laterally substituted dodecyloxy compound has a nematic phase which appears at 205° and lasts for 1°. At 204° a phase transition from nematic to a smectic liquid crystalline phase occurs with relatively high transition energy. Upon further cooling to 157° a third transition is observed and then additional transitions at 133.4° and at 131°. The lowest transition point is at 122°. It can be supercooled easily and has the highest transition energy Fan or mosaic textures that are regarded as typical for smectic liquids disappear upon cooling only at this transition. It is also still possible to shift the coverslide of a sample between glass slides before this transition occurs. Thus the dodecyloxy material without the lateral substitution has five well defined liquid crystalline phases, four of which are smectic. The laterally substituted

TABLE 1

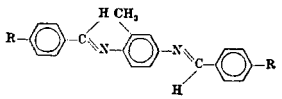


Bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamine

Substituents	Transition temperatures from solid or preceding liquid crystal state to:		
	Nematic (II)‡ °C	Nematic °C	Isotropic °C
R = $CH_3 \cdot O$—	—	131	275.5
$C_5H_{11} \cdot O$—	—	96.8	205
$C_6H_{13} \cdot O$—	—	100	199
$C_8H_{17} \cdot O$—	—	59;56§	179
$C_9H_{19} \cdot O$—	72	96.5	172.5
$C_{10}H_{21} \cdot O$—	66	112.5	166.5
$C_{12}H_{25} \cdot O$—	86.8	131.5	158
$C_{14}H_{29} \cdot O$—	80.5	137.5	149.5
$C_{16}H_{33} \cdot O$—	88	138	143
$C_{18}H_{37} \cdot O$—	93.5	136	137

‡ May be identical with smectic C.
§ Transition from monotropic nematic II.

TABLE 2



Bis-(4′-*n*-alkoxybenzal)-2-methyl-1,4-phenylenediamine

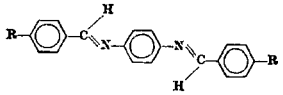
Substituents	Transition temperatures from solid or preceding liquid crystal state to:		
	Nematic (11)‡ °C	Nematic °C	Isotropic °C
R = $C_8H_{16}O$—	—	82	183
$C_9H_{19}O$—	—	81.5	173.5
$C_{10}H_{21}O$—	72	75	170
$C_{12}H_{25}O$—	80	113.5	159

‡ May be identical with smectic C

materials have only two liquid crystalline phases. In Table 1 and Table 2, we have summarized transition temperatures for the laterally substituted derivatives. These may be compared with the transition temperatures of the non-laterally substituted materials which are listed in Table 3. The lowering of nematic to isotropic transition temperatures by lateral substitution can be attributed to the broadening of the molecule.[8] Table 4 lists compounds having halogen terminal substituents.

The compounds in Table 3 have been reported by Gray *et al.*[9] Some of these, the octadecyloxy, dodecyloxy, decyloxy and hexyloxy compound, were prepared by us for comparison purposes. With all these compounds we observed more than one smectic phase. This has already been pointed out in detail earlier for bis-(4′-*n*-dodecyloxybenzal)-1,4-phenylenediamine, which shows four smectic phases. It is in contradiction to the observations of Gray *et al.*,[9] who reported only one smectic phase (see footnote to Table 3). Furthermore, the comparison of corresponding transition temperatures in Table 3 shows that our values are consistently lower than the values of Gray *et al.*[9] Following the common practice in Table 3, all phases below the nematic phase are referred to as smectic, although it is not established that all of them possess a

TABLE 3



Bis-(4′-*n*-alkoxybenzal)-1,4-phenylenediamine

Substituents	Transition temperatures from solid or preceding liquid crystal state to:					
	Smectic 4 °C	Smectic 3 °C	Smectic 2 °C	Smectic 1 °C	Nematic °C	Isotropic °C
$R_1 =$ $CH_3{\cdot}O$—	—	—	—	—	(214.5)‡	> 330‡
$C_5H_{11}{\cdot}O$—	—	—	—	—	175‡	271‡
					171.5‡§	
$C_6H_{13}{\cdot}O$—	—	155	160	168‖	187	255
				(169.5)‡	189‡	259.5‡
$C_8H_{17}{\cdot}O$—	—	—	—	(160)‡	209‡	238‡
$C_9H_{19}{\cdot}O$—	—	—	—	(150.8)‡	211.5‡	228‡
$C_{10}H_{21}{\cdot}O$—	123	140	144‖	163	208	218
			(145.5)‡		212‡	222‡
$C_{12}H_{25}{\cdot}O$—	122	131	134	157	204	205
			(137.5)‡		208‡	209‡
$C_{16}H_{33}{\cdot}O$—	—	—	(127.5)‡	—	—	191‡
$C_{18}H_{37}{\cdot}O$—	—	—	129	147	—	183
			(135.5)‡			187‡

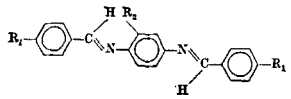
‡ Gray, G. W., Hartley, J. B., Ibbotson, A., and Jones, B., *J. Chem. Soc.*, 4359 (1955). Values in parentheses are the melting points reported by them and are questionable as they appear to correspond with Smectic–Smectic transitions in the similar compounds prepared by us. Calorimetric methods were not employed at that time by these authors and they could, therefore, easily overlook Smectic–Smectic transitions.

§ Transition from monotropic smectic.

‖ DTA curves show here a double peak, which could be due to an additional smectic phase with a range

layered structure. Further work on the structure of these phases is in progress.

TABLE 4



Bis-(4′-halobenzal)-2-substituted-1,4-phenylenediamine

Substituents		Transition temperatures from solid or preceding liquid crystal state to: Nematic °C	Isotropic °C
R_1 = F—	R_2 = H—	175	233.5
Cl—		204‡	290‡
Br—		230§	296§
R_1 = F—	R_2 = CH_3—	152.5	164
Cl—		123	228
Br—		131	217.5
R_1 = F—	R_2 = Cl—	134.8	138.5
Cl—		120.5	216.5
Br—		125	220

‡ Wiegand, Ch., *Z. Naturforsch*, *12b*, 512 (1957).
§ Vorländer, D., Chem. Kristallographie. d. Flüssigkeiten, Leipzig, (1924).

Preparation of Materials

2-*chloro*-1,4-*phenylenediamine* was obtained as a free base from its commercially available sulfate by the normal procedure of first neutralizing its aqueous solution, followed by extraction with some suitable solvents (benzene and ether in this case). After dehydration, filtration and removal of excess of the solvents, the residual liquid on cooling gave a solid which was filtered and recrystallized from chlorobenzene, m.p. 64–64.5 °C, reported m.p. 63–64 °C by Cohen.[10]

2-*methyl*-1,4-*phenylenediamine* was obtained as a free base similarly from its commercially available sulfate except that the residual liquid after removal of excess of the solvents, was distilled under reduced pressure and the fraction, b.p. 166–168°/1–2 mm, was collected. This was recrystallized from chlorobenzene, m.p. 63–64 °C, reported m.p. 64 °C by Nietzki.[11]

1,4-*phenylenediamine* is available commercially.

4-*n-alkoxybenzaldehydes* were prepared with some modifications according to Dickinson *et al.*[12] by dissolving *p*-hydroxy benzaldehyde (1M) in 10% aqueous KOH (1M) solution with subsequent evaporation to almost dryness on a water bath. The solid cake was finely powdered and dried in a vacuum desicator. Potassium salt of this benzaldehyde (1M) was refluxed with an appropriate alkyl bromide (1.47M) in about 200 ml absolute alcohol for 12–14 hours. After removal of most of the alcohol, water was added and an oily liquid separated which was extracted with ether. The ethereal extract after washing a number of times first with 10% aqueous KOH and finally with water was dehydrated over anhydrous sodium sulfate. The residual liquid after filtration and removal of ether was distilled under reduced pressure, when 4-*n*-alkoxybenzaldehydes were obtained in good yields.

Bis-(substitutedbenzal)-phenylenediamines were prepared by refluxing the appropriate diamine (1M) and 4-substituted benzaldehyde (2M) in absolute alcohol for 5–6 hours. The product after isolation was recrystallized several times from appropriate solvents until the transition temperatures remained constant.

The liquid–liquid transitions observed with the purified compounds were sharp and reversible. Differential thermal analysis gave on heating and on cooling within a fraction of a degree equal temperatures for these transitions. Some of the compounds were also analyzed for elemental composition with the following results, calculated values in parentheses:

Bis-(4′-*n*-nonyloxybenzal)-2-chloro-1,4-phenylenediamine:

C, 75.67 (75.65); H, 8.08 (8.52); N, 4.87 (4.64); Cl, 6.00 (5.87).

Bis-(4′-*n*-dodecyloxybenzal)-1,4-phenylenediamine:
C, 80.74 (80.93); H, 10.10 (9.87); N, 4.36 (4.28).
Bis-(4′-*n*-decyloxybenzal)-2-chloro-1,4-phenylenediamine:
N, 4.79 (4.43).
Bis-(4′-*n*-dodecyloxybenzal)-2-methyl-1,4-phenylenediamine:
N, 4.63 (4.20).

Acknowledgement

The authors thank Mr. Y. S. Lee for the determination of the transition energies in Fig. 2.

REFERENCES

1. Leclercq, M., Billard, J. and Jacques, J., Paper at the Liquid Crystal Conference, Kent, Ohio (U.S.A.) 1968.
2. Friedel, G., *Ann. Phys.* **18**, 273 (1922).
3. Sackmann, H. and Demus, D., *Mol. Cryst.* **2**, 81 (1966).
4. Zocher, H., *Z. Physik. Chem.* **132**, 295 (1928).
5. Chatelain, C. R., *Acad. Sci.*, Paris **213**, 875 (1941); *Bull. Soc. Franç. Min.* **66**, 105 (1943).
6. Saupe, A., Plenary Lecture, Liquid Crystal Conference, Kent, Ohio (U.S.A.) 1968.
7. Arnold, H., *Mol. Cryst.* **2**, 63 (1966).
8. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London and New York (1962).
9. Gray, G. W., Hartley, J. B., Ibbotson, A. and Jones, B., *J. Chem. Soc.* 4359 (1955).
10. Cohen, P., *Chemisches Zentralblatt* **1**, 752 (1902).
11. Nietzki, *Ber.* **10**, 1157 (1877).
12. Dickinson, R., Heilbron, I. M. and Irving, F., *J. Chem. Soc.* 1888 (1927).