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New Developments in Liquid Crystal Materials

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New Developments in Liquid Crystal Materials†

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A summary of some new developments in liquid crystal compounds which are of practical interest and at the same time contribute towards understanding the connection between chemical structure and the occurrence of liquid crystal phases is given. Of major importance are combinations of saturated and aromatic ring systems, as well as the effects of substitution in these systems on the transition point from the nematic to the isotropic phase and on other physical properties required for practical use in liquid crystal displays.

1. INTRODUCTION

It is the task of the organic chemist in the field of liquid crystals to find new materials with interesting properties that may be exploited scientifically and economically. The growing interest in low-molecular weight thermotropic liquid crystal compounds in the past 15 years is mostly attributable to the upswing in liquid crystal displays, especially the twisted nematic cell (TNC). Varying requirements are placed upon the physical properties of compounds which are used as components of nematic phases. Important are, among other items, melting point, enthalpy of melting, transition point from nematic to isotropic phase (T_{NI}), optical and dielectric anisotropy, viscosity coefficients, and elastic constants. This paper will deal mainly with new developments in compounds of low molecular weight with ther-

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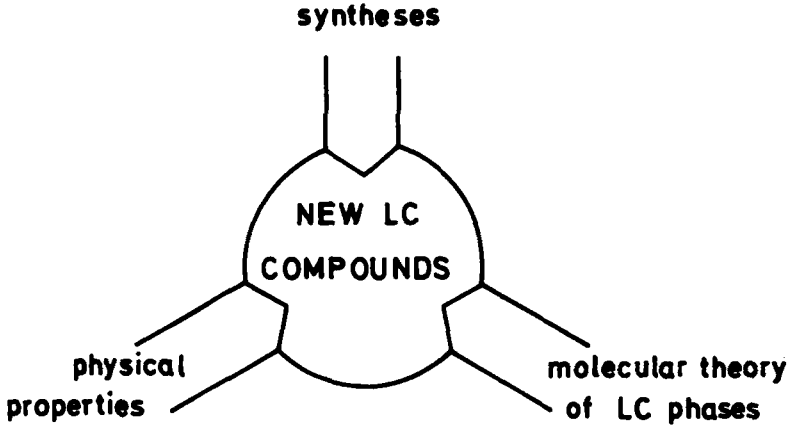
motropic nematic phases, and then it will touch on smectic and discotic compounds as far as they are relevant to practical applications or are of interest in relating mesomorphism with chemical structure.

2. NEMATICS

Figure 1 illustrates the contributions of various fields of knowledge to the development of successful new liquid crystal compounds.



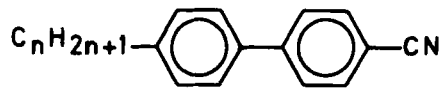
The physical properties and technical properties related to applications have to be translated into molecular terms, as far as this is possible, on a theoretical basis. The target compounds must then be produced using the simplest and most economical syntheses possible. Chemical, especially synthetic problems will not be discussed here. It should, however, be pointed out that particularly high requirements are placed upon the chemical stability of compounds for technical use. One problem with which the synthetic chemist is confronted is the lack of a generally accepted theory able to predict whether a compound—often produced in a large number of synthesis steps—will be a liquid crystal at all. The probability of the compound being an economical success has to date always depended on good "laboratory hypotheses," often provoked by peculiar, but constantly recurring, characteristics of the chemical structures of particularly nematogenic compounds.[1,2]

The presentation of a progress report could limit itself to one of three crucial points, i.e., the technically important physical properties, the characteristics of the chemical structure, or considerations regarding the intermolecular interactions leading to the formation of the nematic phase. It is felt, however, that it is a good way to convey recent synthetic results by looking at the T_{NI} values obtained in the light of different theories and to try to resolve some discrepancies between expectation and results that have occurred in the past. This approach is most promising with molecules which are as simple as possible with respect to their geometry and to the number of heteroatoms involved. It is a fortunate coincidence for this kind of presentation therefore that the technologically most important materials belong to this category. In this way it is also easy to deal in detail with special properties of particularly interesting compounds.

In the past, the work of many synthetic chemists was based on the assumption that essentially two different interactions determine the thermodynamic stability of the nematic phase. There are firstly the dispersion interactions as treated in a simple form in the theory set up by Maier and Saupe.[3] According to this theory, the T_{NI} value is proportional to the polarisability anisotropy of the molecule concerned and inversely proportional to the square of the molecular volume. Secondly, there is the assumption that repulsive forces existing between the molecules—considered as hard rods according to Flory[4]—alone explain the occurrence of a nematic phase. In accordance with this view, a large ratio between the length and diameter of the molecule is favourable for high T_{NI} values. The common influence of both interactions on the stability of the nematic phase has been treated in the generalized van der Waals theory by Cotter.[5]

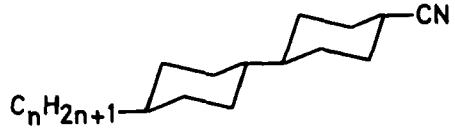
2.1 Directly linked ring systems

The problems of the direct transferability of these theoretical assumptions into chemical structural terms can be illustrated by the examples of the T_{NI} values of the homologues of compound classes *1* to *3* which play an important role in the display industry.



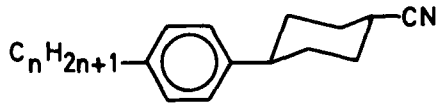
1 n = 3 , C 66 N (26) I (°C)[6]

2 n = 3 , C 43 N 45 I (°C)[7]



3 n = 3 , C 58 S_B (57) N 80 I (°C)[8]

The polarisability anisotropies decrease[9] in the sequence *1>2>3*; the density of the nematic phases[10] decreases in the same order. The order of the T_{NI} values actually observed thus speaks against the nematic behaviour of such compounds being adequately explained by the Maier and Saupe theory. It was therefore suggested[1] than an association of lengthwise extended molecular pairs might lead to a greater effective length in the sequence *3>2>1* giving then the order of the T_{NI} values according to the hard rod theory. However, the fact that molecules like *4*, in which the carbonitrile group is not in conjugation with the aromatic ring, do not form nematic phases is not explained in this simple way. Things become even more unintelligible when the role of the length of the alkyl chain is considered. Thus *1* with n = 1 has a T_{NI} of 45°C, *2* with n = 1 has a T_{NI} of −20°C. This influence of alkyl substitution and of the pattern of alkyl and cyano-substitution of the phenylcyclohexane core on T_{NI} is parallel by the phenylbicyclo[2,2,2]octane system.[13]

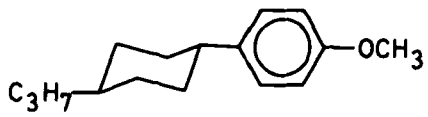


4 n = 3 , C 28 I (°C)[11,12]

The possibility that molecules with two linked 6-membered rings may also form enantiotropic nematic phases, without the assumption of a paired association, can be shown by the example of the two ethers *5*[14] and *6*.[15] These technically very interesting compounds are distinguished by particularly low viscosities ν_{20}^{*}.[16]

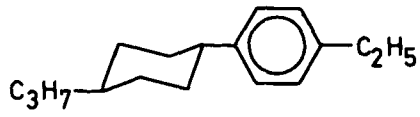
The phenylcyclohexane *5* has proved suitable in broad-range mixtures for twisted nematic cells, and the corresponding bicyclohexyl system *6* is of interest because of its low optical anisotropy (Δn = 0.04).

In the case of molecules with two directly linked rings, we can even go a step further and ask whether markedly polar bonds, as in the case of *5* and *6*, are necessary to all to maintain the nematic phase if the C—O single bond is replaced by C—C single bond. It is interesting that this change has a different effect on the two systems.

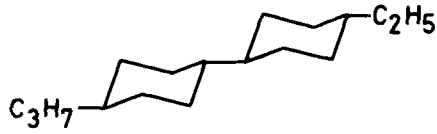


5 C 32 N (10) I (°C), ν^*_{20} = 6 mm²/s

6 C 10 N 17 I (°C), ν^*_{20} = 7 mm²/s



7 C I N [-70]* I (°C)

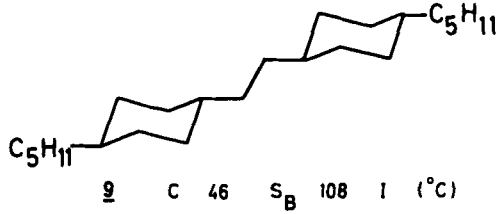


8 C -5 S_B 67 I (°C)

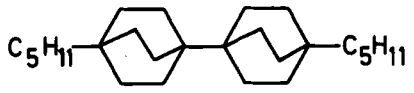
In contrast to *5*, compound *7* has no observable nematic phase. A solution of 10 per cent by weight of *7* in nematic phase 1132 (E. Merck, consisting of type *2* compounds) behaves like a nematogenic compound with a virtual T_{NI} of only −70°C. Compound *8* and its homologues behave completely differently in such mixtures. The virtual

T_{NI} values obtainable by extrapolation lie only a few degrees centigrade below the directly measurable T_{SBI}, even when the content of *8* is raised to 80 per cent by weight.

This result, together with the similar findings with the 1,2-*bis*(*trans*-4-alkylcyclohexyl)ethanes *9*[17,18] and 4,4'-dialkyl-1-1,2-1,1'-dibicyclo[2,2,2]octanes *10*,[19,20] suggests the inclusion of these saturated compounds in any considerations regarding the correlation of chemical structure and T_{NI}, despite the absence of an enantiotropic of monotropic nematic phase.



9 C 46 S_B 108 I (°C)



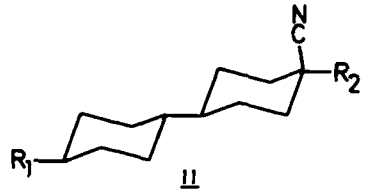
10 C 42 S_B 246 I (°C)

Here it is important to stress that the chemical structure of the nematic matrix used in experiments to obtain virtual T_{NI} values by extrapolation should be as similar as possible to that of the dissolved compounds.

Under this aspect, compounds *5*, *6* and *8* are to be considered as similar in their nematic behaviour—which would be in complete agreement with the hard rod theory. This does not, however, apply to the findings for *7* and its homologues. A simple additional assumption of dispersion interactions according to Maier and Saupe offers no easy solution, because the polarisation anisotrophy *7* is certainly greater than that of *6* and *8*. The possibilities for an explanation which are offered by including any third type[2,21] of intermolecular interaction will not be discussed here.

Since obviously the nematic character of the bicyclohexyl system is only insignificantly influenced by the type of substitution, an axial

carbonitrile group was introduced into the dialkyl bicyclohexyls of type *8*. The nematic compounds *11* are distinguished[22] by their low optical anistropy ($\Delta n \sim 0.03$) and the marked negative anisotropy[23] of the dielectric constants ($\Delta\epsilon = -7$ to -8).



11

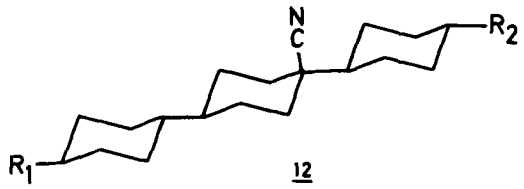
a $R_1 = R_2 = C_5H_{11}$, C 25 S_B 30 N 66 I (°C)

b $R_1 = C_4H_9$, $R_2 = C_7H_{15}$, C 28 S_A 33 N 61 I (°C)

c $R_1 = C_5H_{11}$, $R_2 = C_7H_{15}$, C 20 S_A 38 N 68 I (°C)

Together with their high chemical and photochemical stability, this makes them good basic compounds, especially for displays which are based on the orientation of dichroic dyes in liquid crystal matrices.[24] In the compounds *11*, the carbonitrile groups are sterically well protected so that an association *via* these groups does not seem to be possible. One indication of this is the high dielectric anisotropy (in comparison, $\Delta\epsilon$ of compound *3* is between +4 and +5. Moreover, X-ray structure analyses[25] do not give any indication of pair formation in the crystalline state.

This building principle for nematic compounds seems to be quite viable. For example, compounds *12a* and *12b*[26] represent compound classes which—due to their relatively low melting points and high T_{NI} values—are very well suited as mixing components.

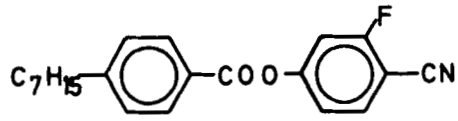


12

a $R_1 = C_5H_{11}$, $R_2 = C_3H_7$, C 69 S_B 154 S_A 156 N 198 I (°C)

b $R_1 = R_2 = C_5H_{11}$, C 33 S_B 176 S_A 185 N 199 I (°C)

The possibility of modifying dielectric anisotropy by different degrees of association of the carbonitrile group has been discussed for some time for nematogenic aromatic compounds.[27,28] Type *13* compounds,[29,30] which show particularly high $\Delta\epsilon$ values and with which the threshold voltage values for the twisted cell are expected to be particularly low, deserve special attention.

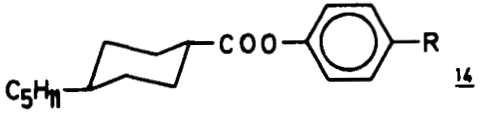


13 C 28.0 N 28.5 I (°C)

2.2 Bridged ring systems

Compound *13* takes us to 2-ring systems with two-membered bridges. In practice, esters of substituted benzoic acids and particularly cyclohexane carboxylic acids have gained importance, not least because they are relatively easy to produce. Compounds *14a* and *14b*,[31] as well as *15*,[32] may serve as examples.

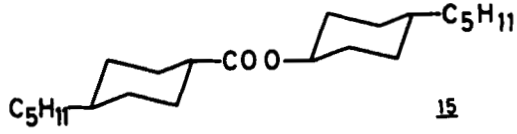
Type *14a* homologues in particular have found wide use because of their low viscosity and their wide nematic temperature ranges. By analogy with bicyclohexyls *6* and *8*, the completely saturated ester *15* proved to be nematic. It is interesting that the nematic character of this grouping is not changed too much by the introduction of an axial carbonitrile group, as shown in *16*.



14

a R = OC_4H_9 . C 49 N 81 I (°C)

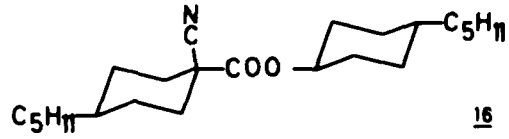
b R = C_5H_{11} . C 37 N 47 I (°C)



15

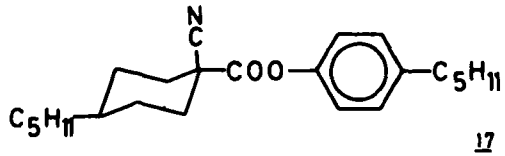
C 51 N 71 I (°C)[32]

Compared with compounds *11a* to *11c*, the dielectric anisotropy of *16*[26] ($\Delta\epsilon = -4$) is less marked. This is attributable to the fact that the dipoles of the N≡C— and O=C< groups have an antiparallel orientation. The low T_{NI} of compound *17* shows that a general transfer of substitution patterns from directly linked compounds to bridged compounds is not possible. This subject will be treated later.



16

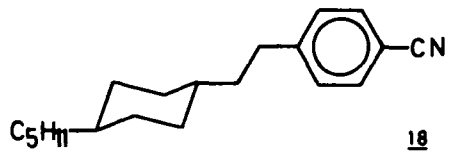
C 11 S_B [10] N 32 I (°C)



17

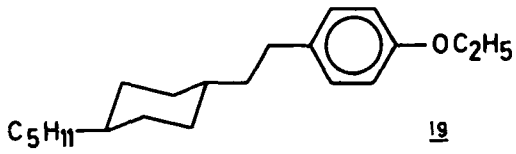
C 32 N [-41]* I (°C)

Linking aromatic or saturated rings *via* —CH_2CH_2— and —OCH_2— bridges has recently become particularly interesting. This often results in compounds showing lower viscosity values than the corresponding esters. Examples *18* to *20* show that the T_{NI} values obtained are quite comparable with those of basic compounds *2*, *3*, and *5*.



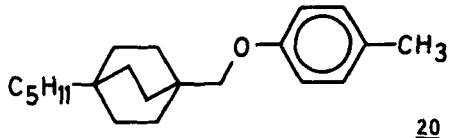
18

C 30 N 51 I (°C)



19

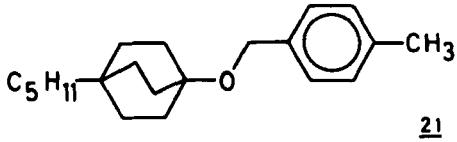
C 18 N 47 I (°C)



20

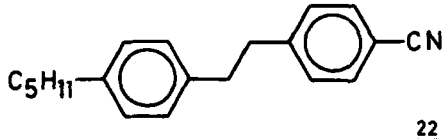
C 60 N [26]* I (°C)

Examples *21*[1] and *22*[33] demonstrate, however, that there are also disadvantageous linking possibilities.



21

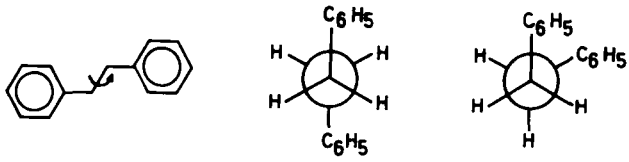
C 63 N [-210]* I (°C)



22

C 62 N [-24]* I (°C)

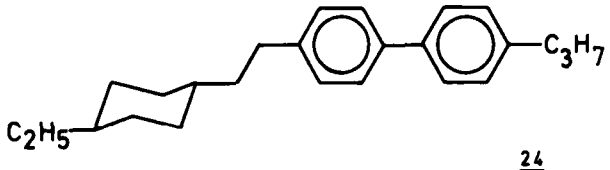
For such clear correlations between chemical structure and nematic behaviour some rules have been formulated by Gray.[1] These regularities also seem to be consistent with the hypothesis set up for molecules with directly linked rings, according to which high T_{NI} values are to be expected for compounds whose molecules exhibit a particularly great continuity of the bonding order along the largest axis of the entire molecule.[2] The transfer of these rules to bridged systems makes sense only if the extended conformation is clearly preferred to other conformations on the grounds of its free energy. The more spherical molecules in any thermodynamic equilibrium affect the T_{NI} as would additions of isotropic compounds. 1,2-Diarylethanes seem not to be advantageous here. ^{13}C-NMR investigations[34] of 1,2-diphenylethanes (*23a*) have shown that at room temperature the ratio of the extended *anti*-form (*23b*) to the *gauche* form (*23c*) is only about 3:2.



23a 23b 23c

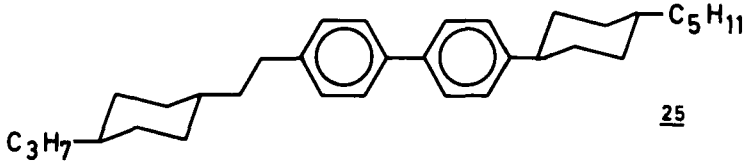
The energentic preference given to the *anti*-form in the case of 1-cyclohexyl-2-phenylethane is probably clearly greater, as shown[35] by preliminary molecular-mechanics calculations.

Compounds with ethyl bridges and more than two rings have recently attracted much attention. The hydrocarbons *24*[36] and *25*[37] have, however, compared with the directly linked compounds *26* and *27*,[38] slightly lower T_{NI} values. The practical value of all these compounds, especially of the homologues of *26* and *27*, lies in the combination of low melting point, high T_{NI}, and comparatively low viscosity.



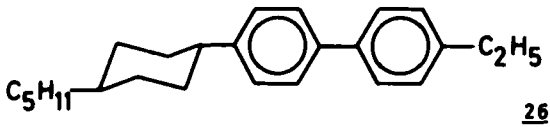
24

C 55 S_B 99 N 122 I (°C)



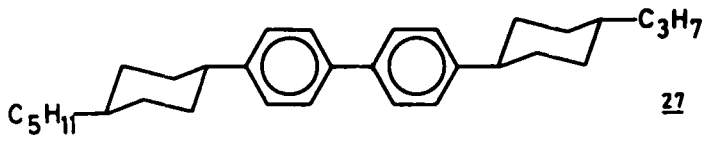
25

C 163 S_B 209 N 274 I (°C)



26

C 34 S_B 146 N 164 I (°C)

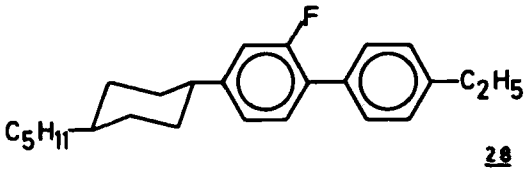


27

C 58 S_B 232 S_A 251 N 311 I (°C)

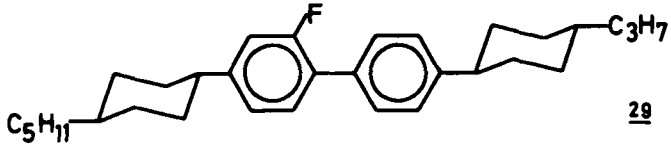
2.3 Aromatic fluoro compounds

At this point I should like to refer to the specific substitution which may be achieved. The modification of some physical properties by substitution in the aromatic rings of nematic compounds has already been described.[39,40] Compounds of type *26* and *27* in mixtures with type *2*, *5*, and *7* phenylcyclohexanes permit nematic temperature intervals between −40 and 100°C to be achieved.[41] It is a general observation that the proximity of a smectic phase in a technical mixture becomes noticeable in the lower temperature range by a particular increase in viscosity, leading to undesirably high switching times in twisted nematic cells. The introduction of an F-atom results in a clear suppression of the smectic phases, as examples *28* and *29*[42] show. This has a favourable influence on the viscosity of mixtures at low temperatures. The twisting of the planes of the two aromatic rings caused by the steric effect of the F-atoms is presumably responsible for the lowering of T_{SN} and—to an acceptable extent—also of T_{NI}. Especially the dispersion interactions responsible for smectic phases may have been diminished due to the reduced conjugation possibilities between the rings.



28

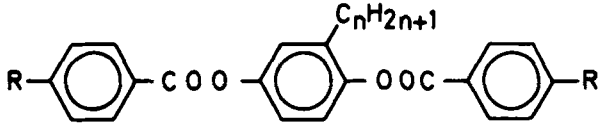
C 37 N 117 I (°C)



29

S_H 68 S_B 154 N 283 I (°C)

In this connection the results obtained by Weissflog and Demus[43] deserve attention. They were able to show that type *30* esters in the sequence from n = 0 to n = 16 are nematic and that smectic phases do not occur with the laterally substitued compounds. The authors attribute this to the steric hindrance in the formation of a smectic layer structure.



30

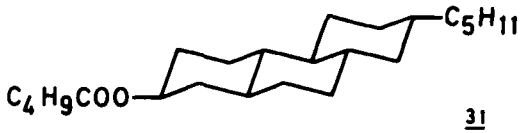
R = alkyl, alkoxy, alkanoyloxy, alkyloxycarbonyloxy

n = 0 to 16

2.4 New nematogenic molecular building elements

Before concluding this section on nematogenic compounds, some new structures should be mentioned which are also of fundamental interest.

Sucrow *et al.*[44] have demonstrated that the perhydrophenanthrene structure, exemplified by *31*, is also a suitable building element for nematic compounds.



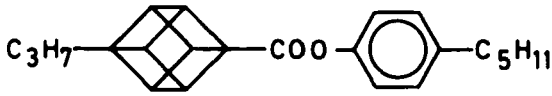
31

C 57 N 76 I (°C)

The nematogenicity of this building element seems to be good in comparison with some disubstituted dihydrophenanthrens.[45]

The 1,4-disubstituted cubanes investigated by Gray *et al.*[46] constitute an important contribution towards the systematics of structure-mesomorphism relationships. Like the 1,4-*trans*-cyclohexylene-, 1,4-phenylene- or 1,4-bicyclo[2,2,2]octylene groups, the 1,4-disubstituted cubane unit permits a rigid linear prolongation of the molecular shape.

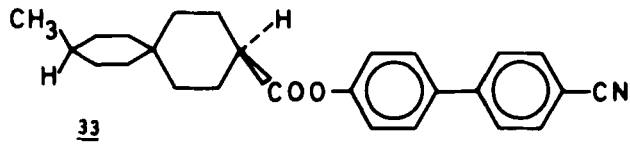
In comparison with the analogous compounds with the other linear groups mentioned, the type *32* compounds have, however, fairly low T_{NI} values. This is attributed to the poor packing and space-filling properties.



32

C 51 N [-60]* I (°C)

The spiro-compounds of Karamysheva *et al.*[47] also constitute a new approach to novel building elements. The T_{NI} of compound *33*, which is relatively low for a 4-ring compound, is probably attributable to the fact that 3,9-disubstituted spiro[5,5]undecanes have a disadvantage compared with the *trans*,*trans*-4,4′-disubstituted bicyclohexyls regarding the spacial arrangement, because the main axes of the substituents are arranged in two different planes orthogonal to each other.



33

C 96 N 162 I (°C)

As expected, systematic investigations[48] of compounds with one-membered bridges, such as —CH_2—, —CO—, —O— and —S—, have led to lower T_{NI} values than in the case of molecules with directly linked rings.

To conclude this chapter on nematic compounds, it remains to be emphasised that the theories mentioned above seemingly do not yet permit a reliable estimation of the T_{NI} on the basis of the chemical structure of a target molecule. Adequate energetic preference for an extended conformation still seems to be the prerequisite for nematic behaviour. For the direct estimation of the influence of the bonding conditions in the molecule on T_{NI}, the criterion of the greatest possible continuity of the bonding order throughout the entire molecule seems to be the most reliable. In this context the paper by Petrzilka[49] de-

serves particular attention; it contains a large number of polar and apolar acetylenic compounds with impressive regularities in the dependence of T_{NI} on the position of the —C≡C— unit in the molecules.

3. SMECTICS

The occurrence of smectic phases in mesogens has mostly been an undesirable event in the industrial synthesis of materials aimed at applications in twisted nematic cells, guest-host displays, or cells for dynamic scattering. This is due to the fact that distinct increases in viscosity can be observed clearly above the transition point T_{NS}. In exceptional cases, such pretransitional effects were advantageous, for example, when the values of the elastic constants K_3 and K_1 could be correlated with special short-range interactions.[50] The technical use of the storage effect in S_A phases[51] and the realization of fast optical switching using ferro-electric S_C phases,[52] have, however, initiated a world-wide search for compounds with such phases.

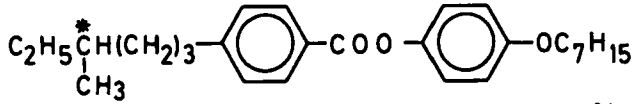
3.1. S_A phases

The estimation of the interactions leading to the formation of a smectic S_A phase is certainly more difficult than in the case of nematic phases. A specific synthesis of compounds with S_A phases is furthermore made more difficult by the extensive polymorphism of smectic phases. The type of smectic phase—9 well-described phases are known—is extremely dependent on small deviations in the molecular structure.[1] 4′-Octylbiphenyl-4-carbonitrile (*1*, n = 8) with T_{CS_A} 22°C, T_{S_AN} 34°C, T_{NI} 41°C is a basic substance which has proved suitable in ready-to-use mixtures. It possesses some properties advantageous for the storage effect, a high optical anisotrophy favourable for reading contrast, as well as a high dielectric anisotrophy. Interestingly, the tendency towards formation of an S_A phase seems to continue with growing chain length, as the transition points of the dodecyl derivative (*1*, n = 12) show:[53] T_{CS_A} 48°C, T_{S_AI} 59°C. The phenylcyclohexanes (*2*) are considered as compounds with marked nematic properties. An S_A phase, however, was recently found in 4-*trans*-(dodecyclohexyl)benzonitrile:[54] T_{S_AN} 51°C, T_{NI} 61°C. In comparison, *trans*, *trans*-4′-dodecylbicyclohexyl-4-carbonitrile (*3*, n = 12) has no detectable S_A phase (T_{CN} 68°C, T_{NI} 78°C, the nematic phase being supercoolable to room temperature.[55]

In this context, the increased occurrence of S_A phases in type *11* and *12* compounds with their strong permanent dipoles almost vertical to the longitudinal axes should be pointed out.

3.2 Chiral S_C phases

The basic investigations into the possibility of using ferro-electric chiral S_C phases were carried out with the two Schiff's bases: *N*-(*p*-decycloxybenzylidene)-*p'*-amino-2-methylbutylcinnamate (DOBAMBC) and *N*-(*p*-hexyloxybenzylidene)-*p'*-amino-2-chloropropylcinnamate (HOBACPC).[52,56] Both compounds are not very stable and proved to be difficult to handle because of their high melting points. Nevertheless, the physically convincing results obtained with these substances will no doubt initiate a systematic search for low-melting chiral compounds with an S_C phase. Type *34* esters[57] may be considered as a first step towards the aim. Also the recently discussed possibility of using smectic phases with ferro-electric properties other than S_C opens up another interesting field for synthetic chemistry.



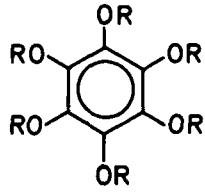
34

C 30 S_C^* 46 N^* 63 I (C)

4. DISCOTIC PHASES

Since Chandrasekhar[58] discovered that flat disc-shaped molecules can have mesomorphic properties, many compounds have been found which show these so-called discotic phases. The various phases have been classified.[59]

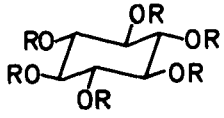
Compounds with discotic phases have not yet gained practical importance in display techniques, although the basic possibility of a twisted discotic cell,[60] analogous to the twisted nematic cell, has been demonstrated. The high viscosity of the disc-like nematic phase available to date is probably one of the reasons for the fact that such a technique has not become an established method.



35

$R = COC_nH_{2n+1}$

n = 7, C 81 D 87 I (°C)



36

$R = COC_nH_{2n+1}$

n = 7, C 76 D 199 I (°C)

In this context it is interesting that the development of discotic compounds, in view of their chemical structure, seems to take the same course as that of nematic compounds. Thus the class of hexa-*O*-alkanoyl derivatives of inositol *36*, recently found by Praefcke,[61] show a clearly wider temperature interval of the mesophase than the corresponding[58] aromatic compounds *35*.

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