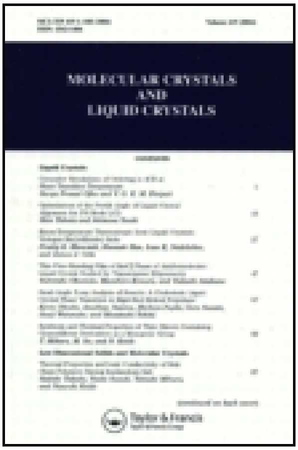


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Comments on Some Recent Developments in the Field of Liquid Crystals

G. W. Gray [a]
[a] Department of Chemistry, University of Hull, Hull, Hu6 7RX, UK

To cite this article: G. W. Gray (1981): Comments on Some Recent Developments in the Field of Liquid Crystals, Molecular Crystals and Liquid Crystals, 63:1, 3-17

To link to this article: http://dx.doi.org/10.1080/00268948108071984

Mol. Cryst. Liq. Cryst., 1981, Vol. 63, pp. 3–18
0026-8941/81/6304–0003 $06.50/0

Printed in the U.S.A.

Comments on Some Recent Developments in the Field of Liquid Crystals†

G. W. GRAY
Department of Chemistry, University of Hull, Hull, HU6 7RX, UK

(*Received June 30, 1980*)

Three areas of research into liquid crystals which have seen considerable development since the last International Liquid Crystal Conference at Bordeaux in 1978 have been selected for a brief over-view.

These areas concern:

1) *New Liquid Crystal Materials* containing non-aromatic ring systems and the developments which have followed from the earlier studies of esters of *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids and the *trans*-4-*n*-alkyl-1-(4′-cyanophenyl)cyclohexanes (PCH's).

2) *Agreement over a Nomenclature Problem Concerning Smectic Polymorphs* and some interesting features of the smectic phase sequences for the 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines.

3) *Discotic Phases*—the discovery that the historically well known mesophase of di-isobutylsilandiol is a discotic liquid crystal phase and the progress being made in studies of other discotic systems.

INTRODUCTION

Having been invited to give this opening lecture† which I judged would be attended by people with a spectrum of interests in the field of liquid crystals, I felt that it would be presumptious of me to choose one single theme, since that theme might be of direct interest to only a few of those present.

On the other hand, a rather diffuse talk of general interest did not appeal too much to me.

A compromise developed, as a result of which I have chosen to talk about

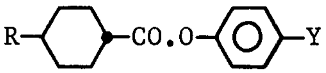
---

† Invited lecture presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

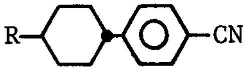
three topics of considerable importance, and so I hope to say something of interest to most of those present.

1 Liquid crystal materials containing alicyclic ring systems

Non-aromatic or partially aromatic mesogens containing alicyclic ring systems have attracted much interest since the earlier work on esters[1] such as (I) and PCH materials[2] of structure (II).



(I)

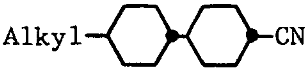


(II)

Mentioning only two features of such materials which make them of value in different applications, we have

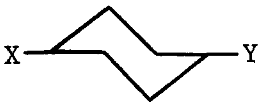
a) their low birefringence,

b) the combination of positive dielectric anisotropy ($\Delta\varepsilon$) and negative diamagnetic anisotropy ($\Delta\chi$) which can be found for nematogens such as (III)–the CCH materials[3]

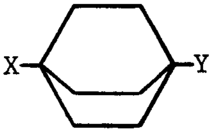


(III)

Compounds (I), (II), and (III) contain the trans-1,4-disubstituted cyclohexane ring system (IV). This alicyclic ring system and the 1,4-disubstituted bicyclo[2.2.2]octane ring system (V) are the two non-aromatic ring structures that so far have attracted most attention.

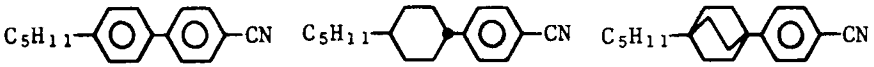


(IV)



(V)

As the number of mesogens containing these ring systems has increased,[4] it has become obvious that their T_{N-I} values are usually higher than those of the fully aromatic analogues. For example:



T_{N-I} (°C) 35 55 100

This trend of decreasing T_{N-I} in the sequence

Bicyclo-octane (BCO) > Cyclohexane > Benzene

is now established for *eleven* different systems (see Table I, Section A).

In a further *four* cases (see Table I, Section B), for which data on the benzene analogues are not yet available, the order of decreasing T_{N-I} is

BCO > Cyclohexane

In only two cases is there a partial inversion of the order to

BCO > Benzene ⩾ Cyclohexane

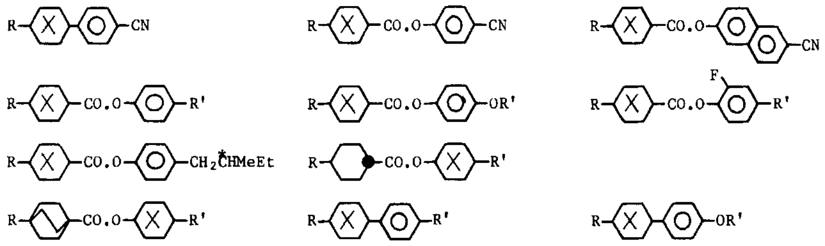
see Table I, Section C, and in these two cases we are dealing with rather high T_{N-I} values at which conformational changes in the flexible cyclohexane ring may play a significant role in disturbing the nematic order.[5]

Details of the materials listed in Table I to illustrate the systems we have been studying will be given either in papers presented during this conference —one of which will discuss the orders of T_{N-I} that have been found—or to be published in the near future.

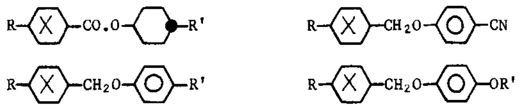
TABLE I

Orders of decreasing T_{N-I} for some related systems (R = alkyl) in which ring X may be benzene, cyclohexane, or bicyclo[2.2.2]octane (BCO)

A. BCO > Cyclohexane > Benzene



B. BCO > Cyclohexane

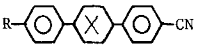


C. BCO > Benzene ⩾ Cyclohexane

For the present, it is sufficient to note that high T_{N-I} values for BCO compounds,[4] and to a lesser extent for the cyclohexane analogues, arise for a large enough number of materials of sufficiently different structural types for us to consider whether this represents the general situation and whether any other systems for which the above orders are not observed may not be exceptional for some reason(s).

Let us look at some exceptions that have been reported. In each case, ring X may be benzene, cyclohexane, or bicyclo[2.2.2]octane; R = alkyl.

(1)

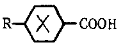


Benzene > BCO[5]

(2)

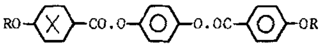
Benzene > BCO > Cyclohexane[6]

(3)



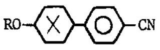
Benzene > Cyclohexane[7]

(4)



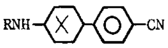
Benzene > BCO[6] - order applies also when both end rings are changed

(5)



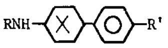
Benzene > BCO[8] - note that no liquid crystal properties have been reported for X = Cyclohexane

(6)



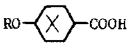
Benzene > Cyclohexane[9]

(7)



Benzene > Cyclohexane[9]

(8)

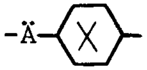


Benzene >> Cyclohexane[10]

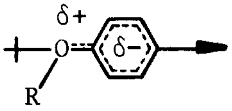
In cases (1) and (2), we have replacement of the central ring of a three ring system by a BCO ring, resulting in some decrease in T_{N-I} (28° in case (1) and 50° in case (2)). This may be because the bulk of the BCO ring in the middle makes the molecule somewhat barrel-shaped, i.e., the molecules deviate towards a more spherical shape, and this may be unfavourable to nematic ordering.

In case (3), the effects are quite small—for R = n-C_6H_{13}, the decrease in T_{N-I} is from 115° to 96.4° (18.6°) on passing from benzene to cyclohexane. High T_{N-I} values are not therefore involved, but the systems are somewhat special in the sense that the liquid crystal properties depend on the dimer structure, as well as on the rest of the molecular structure. The m.p.s. of the BCO analogues are higher than the T_{N-I} values of the benzoic or cyclohexane acid analogues, e.g., R = n-C_6H_{13}, C—I, 157°—little supercooling of the melt, and in the absence of virtual T_{N-I} values, the position of BCO in the order cannot be predicted.

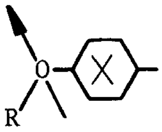
However, in the five remaining cases—(4) to (8)—we have the common feature of an atom with at least one lone pair of electrons (atom A = 0 or N) located next to ring X, i.e.,



Now, when X = benzene (the aromatic case), conjugative interactions between A and the ring may occur, and alter the dipolar situation significantly. Thus, for the aromatic ether, we will have structural contributions from a resonance situation represented by (VI), whereas in the cyclohexane or BCO analogue, the position may be represented simply as in (VII). The dipole moment is therefore changed on passing from (VI) to (VII) from along the molecular long axis to across it.

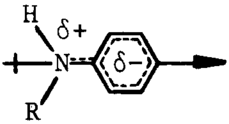


(VI)

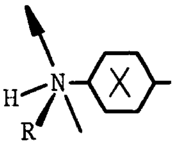


(VII)

The same argument will also apply for the amino compounds—see structures (VIII) and (IX).



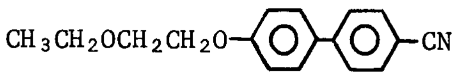
(VIII)



(IX)

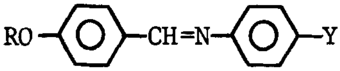
In five cases therefore, the cross dipole arising from unconjugated RO- or RNH-functions in the alicyclic system could be less favourable to nematic properties, and explain the observed order of T_{N-I} – Benzene > Cyclohexane/BCO. Conversely, the more axial dipole in the aromatic system, by enhancing the anisotropy of the system, may be particularly favourable to nematic properties.

However, the adverse effect of unconjugated ether functions is not a novel situation, and has been observed in other contexts when extra ether linkages are incorporated in the carbon chains of alkoxy groups. For example, the compound[11]



has a C—I value of 75.5° and a virtual T_{N-I} of [$-15°$], a decrease in T_{N-I} of 93.5° from the compound with a $CH_3(CH_2)_4O-$ terminal group.

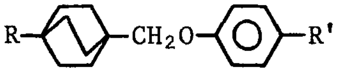
Similarly, Dietrich and Steiger[12] studied Schiff's bases of structure



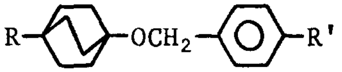
in which R was a chain of carbons incorporating *additional* ether linkages. The T_{N-I} values were always lower and often much lower in the compounds containing one or more additional CH_2OCH_2 groups and they wrote "methylene substitution by an atom which possesses a permanent dipole (unless adjacent to the phenylene) results in a destabilization of all phases..."

The unconjugated CH_2OCH_2 group will again contribute a cross dipole to the molecular structure.

A further very striking example of this kind is provided by compounds[13] (X) and (XI).



(X)

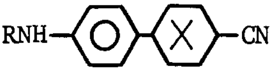


(XI)

The aryl ether (X) with R = n-C_5H_{11}, R′ = CH_3 has a m.p. of 69° and a virtual T_{N-I} of [26°]. The reversed aliphatic ether (XI), with R = n-C_5H_{11}, R′ = CH_3 has a m.p. of 63° and a virtual T_{N-I} of [$-210°$]. This striking case strongly reinforces example (5)—where with X = BCO, the pentyloxy compound has a virtual T_{N-I} below room temperature—and (8) where the cyclohexane acids with alkoxy groups are often liquids showing no sign of nematic phases.

Osman and Revesz[9] attributed the markedly lower T_{N-I} values of their cyclohexylamino compounds (cases (6) and (7)) to another reason. They note that the (*e*, *e*) conformer, which is most favourable to nematic properties, is able to change through twist and boat forms to the unfavourable (*a*, *a*) conformer, but that the conformational free energy difference—ΔG_x° has an appreciable temperature dependence and this will determine both the rate of inversion and the amount of the "anti-nematic" (*a*, *a*) conformer. They give an order of $-\Delta G_x^\circ$ values in which —OR, —NHR, and —CN groups are low in conformational energy, and use this to explain the low T_{N-I} values in cases (6) and (7). Presumably they would also use this explanation for the low T_{N-I} values in the case of compounds with an —OR group on the cyclohexane ring.

Although these considerations may play a part, one doubts that this is the whole story, because we know that RO— attached to the *rigid* BCO ring adversely affects T_{N-I} values, and here no conformational inversion can occur. Moreover, although the low position of —CN in the conformational energy order explains the low T_{N-I} values of Osman and Reversz's[9] compounds of structure (XII)



Benzene > Cyclohexane

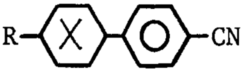
(XII)

it does *not* explain the fact that the T_{N-I} values of CCH compounds (XIII)

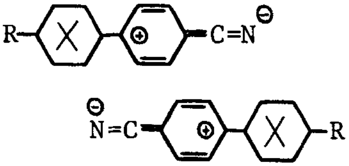
(XIII)

may be *higher* than those of the analogous PCH compounds, e.g., CCH (XIII) R = C_3H_7, T_{N-I}, 80°; PCH analogue, T_{N-I}, 46°.

Whilst there is no firm answer to this problem, one can propose some thoughts about it. In systems of structure

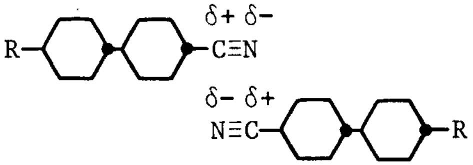


when X = benzene, S_A phases are known to have an interdigitated bilayer structure,[14] and the tendency to molecular pairing (XIV) also occurs in the nematic phases when X = benzene,[14] cyclohexane,[15] and BCO.[15] The pairing is such that dipolar repulsions between neighbouring cyano groups are minimized by their location near to the inter-ring bond of a neighbouring molecule. This can be related to the conjugation of the cyano group with the benzene ring, resulting in delocalization of charge from the C of the CN group onto the far carbon of the aromatic ring. With the molecular pairing, we now have a favourable, attractive charge distribution (XIV) in the system.



(XIV)

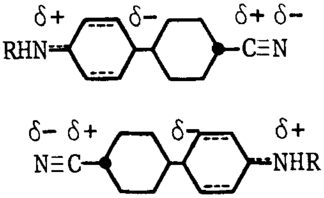
This conjugation cannot occur in a CCH compound and the charge distribution of the CN group is fixed as shown in (XV). Interestingly, CCH compounds give S_B phases in which the molecules are paired as shown (XV), with oppositely aligned, neighbouring cyano groups.[15]



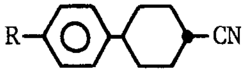
(XV)

If this type of molecular pairing persists in the nematic phases of the CCH compounds, then the effective unit is longer than that in (XIV), and may account for the higher T_{N-I} values. So far, supporting evidence for this pairing (XV) in the nematic phase has been difficult to obtain, although a weak diffraction peak (R = n-C_7H_{15}) indicates that the association occurs, but weakly.[15]

If these reasonings are correct, then, to rationalize Osman's results, this type of molecular pairing (XV) would have to be disfavoured for the compounds (XII). Indeed, it is possible that this is the case, bearing in mind the charge distribution resulting from the RNH group conjugated with the benzene ring. This could lead to a pairing situation of the type shown below and involving a shorter unit.



However, such arguments can be applied with less confidence to explain the low nematic tendencies of systems such as



and the conclusion one must reach is that the relative nematic tendencies of benzene and cyclohexane systems are probably governed by a combination of factors stemming not only from attractive/repulsive interactions between neighbouring groups and conformational effects involving the cyclohexane ring, but also from steric factors which determine the efficiency of packing of neighbouring molecules. The relative importance of these different effects may vary from system to system and thereby influence the observed orders of T_{N-I}. The elucidation of these problems is a considerable challenge to the physical-organic chemist.

2 Smectic systems

Over the past few years, considerable confusion has arisen concerning the lettering system designating different polymorphic smectic phases. Professor Sackmann and I, together with Dr. Demus and Dr. Goodby were very conscious of this and prior to the European Conference at Garmisch-Partenkirchen in January this year, we discussed the position thoroughly.

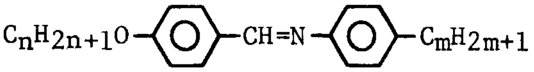
The historical situation has been reviewed in a lecture I gave at that meeting, and this will be published[16] in the proceedings. For the present purposes, only the following need be said. Following

i) evidence obtained over several years and eventually published[17] by Goodby and myself that tilted S_B phases and orthogonal S_B phases are immiscible;

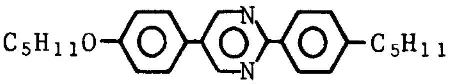
ii) the substantiation of this fact by Sackmann;[18]

iii) the discovery by de Jeu and de Poorter[19] and by Doucet and Levelut[20] that direct tilted to orthogonal S_B transitions may occur in pure compounds, a different code letter from B was clearly needed for the tilted analogues of B phases.

As a result of work by de Vries and Fishel[21] on the n0.m (XVI)–40.2, published in 1972, many workers, including ourselves chose to use S_H. However, the Halle group chose S_G, because they had demonstrated that the new S_G phase they had earlier (1971) observed in the pyrimidine[22] (XVII) was miscible with the relevant phase of 40.2.



(XVI)



(XVII)

The letter G clearly has historical priority, and Demus, Goodby, Gray, and Sackmann[23] have recommended that to avoid further confusion, tilted S_B phases previously called S_{B_C} or S_H phases, should be coded as S_G. Conversely, S_H should now be used to code these phases hitherto described by those outwith the Halle group as S_G. If this recommendation is adopted, further confusion over the duality of nomenclature which has existed will hopefully be avoided. To summarize what this means, let us look at two well known compounds:

TBBA:	
Recommended lettering	H, G, C, A, N, Isotropic
Replacing	G, H, C, A, N, Isotropic
Pyrimidine (XVII)	
Recommended lettering	G, F, C, A, Isotropic
Replacing	H, F, C, A, Isotropic

It should be noted that the above way of presenting phase sequences, i.e., omitting the symbol S for smectic, requires that we denote Isotropic as such, or perhaps by Iso, but not by I, because this now represents the new S_I phase discovered by the Halle group[24] in TBDA, for which the sequence is

G, F, I, C, A, Isotropic

This mention of a new smectic phase leads me to correct the situation for the compound

Goodby and I tentatively suggested in 1979[25] that this compound might possess two new smectic phases which we lettered J and K and gave the sequence

K, H, G, J, F, C, N, Isotropic

At that time we had *no* x-ray evidence to support the case, and our arguments were based on the following points:

i) reversible transitions were observed by thermal analysis and optical microscopy for seven transitions;

ii) the observed textures of the "new" phases were unlike those of any smectic phase hitherto studied;

iii) the phase lettered K was very fluid;

iv) miscibility evidence;

v) reports by earlier workers that four or five smectic phases had been observed.[26]

Recently however, Leadbetter *et al.*[27] have been able to do x-ray work on this compound, and it is now clear that the sequence of phases is simpler and should be

H′, G′, I, C, N, Isotropic

Leadbetter will say something more about this in a paper he will present at this meeting, but having been responsible for the suggestion that two new smectic phases may exist, I wanted to be the first to correct the situation.

It is interesting that the G′ texture is different from that of other G phases, and that the phase we took to be G turns out to be smectic H′, but has a texture quite unlike H phases. Also the mobility of the K phase, which is in fact a solid, is of interest.

We now understand where our miscibility evidence was in error and will publish a reappraisal of the situation in the near future. This situation clearly spells out the dangers of phase diagnosis without proper supporting x-ray evidence.

And so the situation is that polymorphic smectic phases are currently restricted to nine, A to I.

It is of course a matter for current debate how many of these phases should be classed as real smectic phases, and how many should be thought of as crystals, because several of these phases have a three-dimensional structure. My own view is that the question is of theoretical interest, but not a basis for dissent, because all these phases, A to I, whether we call them smectics, crystals, or anything else, are extremely interesting and still present us with many unsolved problems.

Let us consider but two of these.

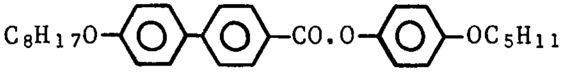
a) Defining S_B phases as phases in which the average alignment of the molecules in the layers is hexagonal close packing, and the long axes are approximately orthogonal to the layers, giving optical uniaxial properties, the extent of correlation between layers was first investigated by Leadbetter, Frost, and Mazid.[28] From this work and its development by the Exeter group and others such as Moncton and Pindak,[29] using a range of materials including n0.m's (XVI), it is clear that various stacking arrangements of the layers are possible.

In the n0.m's, three types occur—AAA--- (monolayer); ABA--- (bilayer); and ABCA--- (trilayer), and that this stacking arrangement may change within the temperature range of the B phase.[16,28,30,31] For example, for 50.7 the changes

bilayer → trilayer → bilayer

occur with decreasing temperature within the three-dimensional phase.

However, as first pointed out by Leadbetter *et al.*,[28] in several cases such as

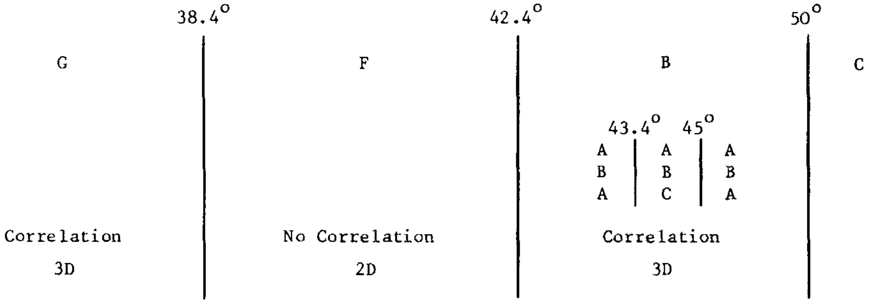


the S_B phase behaves as though it has almost no correlation between the layers. Subsequent studies have confirmed that such 2D smectic B phases exist and are probably fairly common. Here we have the problem. Since the new I phase appears to be an uncorrelated or 2D smectic G phase, but is not miscible with the 3D smectic G phase and is indeed separated from it in phase sequences such as I, F, G, we must now ask whether correlated and uncorrelated B phases are also separate phase types? If they are, they should be immiscible, and yet to my knowledge, immiscibility of 2D and 3D B phases remains unproven.

b) Still on the question of interlayer correlation or non-correlation, work on n0.m's, particularly on 50.6, has thrown up another interesting set of observations. For 50.6 we have[16,28,30,31]

$$\text{Cryst} \xrightarrow{36^\circ} \text{G} \xrightarrow{38.4^\circ} \text{F} \xrightarrow{42.4^\circ} \text{B} \xrightarrow{50^\circ} \text{C} \xrightarrow{51.8^\circ} \text{A} \xrightarrow{60.3^\circ} \text{N} \xrightarrow{72.8^\circ} \text{Isotropic}$$

Looking at the lower temperature phases only, we have



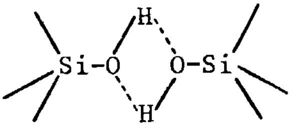
This illustrates the stacking changes in the B phase, and it is noted that although the bilayer stacking is regained just above the transition to the F phase, the *lower* temperature bilayer stacking is *more* disordered than that above 45°.

Lower temperatures do not therefore necessarily mean *increasing* order, and this point is made even more dramatically when we realize that the 3D order of the B phase is *lost* when the F phase forms on *cooling*, and is regained only in the G phase at 38.4°. Thus an F phase with weakly coupled 2D layers lies on the temperature scale *intermediate* between the B and G phases with 3D order. As shown by Leadbetter *et al*,[16,28,30,31] the B–F transition occurs when the amplitude of transverse modulations associated with undulation modes in the B phase becomes critical, and a stable, tilted structure, lacking interlayer correlation, is formed.

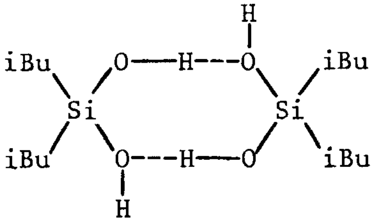
3 Discotic phases

As we know, Chandrasekhar[32] and his group initiated developments in this new area of liquid crystal work by their discovery of discotic phases in hexa-acyl derivatives of hexahydroxybenzene. The columnar stacking of disc-like molecules in derivatives of triphenylene has also been studied extensively by Billard,[33] and in collaboration with Levelut and other groups in France, important studies[34] leading to the recognition of different polymorphic modifications of the discotic phase have been carried out. Publication of Billard's lecture[35] on Discotic Phases at Garmisch-Partenkirchen is to be awaited with great interest.

I simply wish to draw attention to work done recently at Leeds, Sussex, and Hull Universities on the thermotropic mesophase of di-isobutylsilandiol which has presented an unsolved problem for over 25 years. First discovered in 1952 by Eaborn,[36] and examined in some detail by Eaborn and Hartshorne[37] in 1955, the unusual optical textures of the phase formed between 89.5° and 101.5° did not match those of any other known phase in the liquid crystal class, and its negative uniaxial properties were puzzling. A misleading factor it now transpires was the hydrogen-bonding arrangement (XVIII) proposed by Kakudo and Watase.[38] However, new work and a reappraisal of the single crystal x-ray diffraction data suggest[39] that the basic unit is probably as shown in (XIX).



(XVIII)



(XIX)

The two isobutyl groups give the dimer the shape of a square slab. Models suggest that these slabs can stack one above the other forming a tilted column, enabling further hydrogen bonding to occur along the stack axis. The crystal-discotic transition is thought to occur through weakening of the hydrogen bonds along the stack axis allowing the formation of untilted columns of the slab-like dimers. These columns then constitute the units of the hexagonal packing in the discotic phase.

The discotic-isotropic liquid transition probably occurs through a breaking of the hydrogen bonds within the dimers. Weakening or breaking of equal numbers of hydrogen bonds is involved at both transitions, and not surprisingly, both have similar enthalpies.

It is interesting that no other related diol —$R_2Si(OH)_2$— forms this phase, and that only the isobutyl group seems to be suitable. Many other groups have been tried—different alkyl groups, cyclohexyl groups, and systems in which two different R groups are used. None has so far given a phase. Again, models suggest that isobutyl groups are just the right size to give a stable stacking of the molecules and to fill space efficiently. Larger or smaller groups either make stacking difficult or leave empty spaces.

This work was first reported briefly at Garmisch-Partenkirchen,[39] and a more detailed paper is in the process of publication.[40] The microscopic textures of the phase are very similar to those of other discotic phases formed by the esters of hexahydroxyphenol and the derivatives of triphenylene; the discotic phases of the esters are miscible with that of the diol.

And so, a phase which has been known for over 25 years now fits into the most recent category of liquid crystal phase to be discovered, and no longer presents a classification problem.

CONCLUDING REMARKS

It is hoped that what has been said on these topics is of value and interest, and that the review of these areas has set the scene for a highly successful conference.

References

1. H.-J. Deutscher, F. Kuschel, S. Konig, H. Kresse, D. Pfeiffer, A. Wiegeleben, J. Wulf, and D. Demus, *Z. Chem.*, **17**, 65 (1977); H.-J. Deutscher, B. Laaser, W. Dolling, and H. Schubert, *J. prakt. Chem.*, **320**, 194 (1978).
2. R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, *Angew. Chem. Intern. Ed. Engl.*, **16**, 100 (1977); L. Pohl, R. Eidenschink, J. Krause, and L. Pohl, *Phys. Lett.*, **60A**, 421 (1977).
3. L. Pohl, R. Eidenschink, J. Krause, and G. Weber, *Phys. Lett.*, **65A**, 169 (1978).
4. G. W. Gray and S. M. Kelly, *J. Chem. Soc. Chem. Commun.*, 974 (1979); *Angew. Chem. Intern. Ed. Engl.*, in press; *J. Chem. Soc. Chem. Commun.*, 466 (1980).
5. D. G. McDonnell, Ph.D. Thesis, University of Hull (1979).
6. M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970); *J. Amer. Chem. Soc.*, **92**, 1582 (1970); M. J. S. Dewar, A. C. Griffin, and R. M. Riddle, *Liquid Crystals and Ordered Fluids* (J. F. Johnson and R. S. Porter, eds), Vol. 2, p. 733, Plenum, New York, 1974; M. J. S. Dewar and R. M. Riddle, *J. Amer. Chem. Soc.*, **97**, 6658 (1975); M. J. S. Dewar and A. C. Griffin, *J. Amer. Chem. Soc.*, **97**, 6662 (1975).
7. H. Schubert, R. Dehne, and V. Uhlig, *Z. Chem.*, **12**, 219 (1972).
8. G. W. Gray, *Advances in Liquid Crystals for Applications*, B.D.H. Special Publication, B.D.H. Chemicals Limited, Poole, Dorset, BH12 4NN, England (1978).
9. M. A. Osman and L. Revesz, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 133 (1980).
10. H.-J. Deutscher, B. Laaser, W. Dolling, and H. Schubert, *J. prakt. Chem.*, **320**, 194 (1978).

11. G. W. Gray and A. Mosley, hitherto unpublished results.
12. H. J. Dietrich and E. L. Steiger, *Mol. Cryst. Liq. Cryst.*, **16**, 263 (1972); E. L. Steiger and H. J. Dietrich, *Mol. Cryst. Liq. Cryst.*, **16**, 279 (1972).
13. N. Carr, G. W. Gray, and S. M. Kelly, to be published.
14. A. J. Leadbetter, R. M. Richardson, and C. N. Colling, *J. Phys.* (*Paris*), **36**, 37 (1975).
15. A. J. Leadbetter, private communication.
16. J. W. Goodby, G. W. Gray, A. J. Leadbetter, and M. A. Mazid, Proceedings of the European Conference held at Garmisch-Partenkirchen, January, 1980.
17. J. W. Goodby and G. W. Gray, *J. Phys.* (*Paris*), **40**, 363 (1979).
18. H. Sackmann, *J. Phys.* (*Paris*), **40**, 5 (1979).
19. W. H. de Jeu and J. A. de Poorter, *Phys. Lett.*, **61A**, 114 (1977).
20. J. Doucet and A.-M. Levelut, *J. Phys.* (*Paris*), **38**, 1163 (1977).
21. A. de Vries and D. L. Fishel, *Mol. Cryst. Liq. Cryst.*, **16**, 311 (1972).
22. D. Demus, S. Diele, M. Klapperstück, V. Link, and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **15**, 161 (1971).
23. D. Demus, J. W. Goodby, G. W. Gray, and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 311 (1980).
23. H. Sackmann, lecture presented at the European Conference held at Garmisch-Partenkirchen, January, 1980, to be published.
25. E. M. Barrall II, J. W. Goodby, and G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 319 (1979).
26. S. L. Arora, T. R. Taylor, J. L. Fergason, and A. Saupe, *J. Amer. Chem. Soc.*, **91**, 3671 (1969); D. Demus and R. Rurainski, *Mol. Cryst. Liq. Cryst.*, **16**, 171 (1972); W. Spratte and G. M. Sneider, *Mol. Cryst. Liq. Cryst.*, **51**, 101 (1979).
27. A. J. Leadbetter, private communication.
28. A. J. Leadbetter, J. C. Frost, and M. A. Mazid, *J. Phys.* (*Paris*), **40**, 325 (1979).
29. D. E. Moncton and R. Pindak, *Phys. Rev. Lett.*, **43**, 701 (1979).
30. A. J. Leadbetter, M. A. Mazid, B. A. Kelly, J. W. Goodby, and G. W. Gray, *Phys. Rev. Lett.*, **43**, 632 (1979).
31. A. J. Leadbetter, M. A. Mazid, and R. M. Richardson, presented at the Liquid Crystal Conference, Bangalore, December, 1979, to be published.
32. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana*, **9**, 471 (1977).
33. A. Beguin, J. Billard, J. C. Dubois, N. H. Tinn, and A. Zann, *J. Phys.* (*Paris*), **40**, 15 (1979).
34. Papers presented at the European Conference held at Garmisch-Partenkirchen, January, 1980, to be published.
35. J. Billard, lecture presented at the European Conference held at Garmisch-Pertenkirchen, January, 1980, to be published.
36. C. Eaborn, *J. Chem. Soc.*, 2840 (1952).
37. C. Eaborn and N. H. Hartshorne, *J. Chem. Soc.*, 549 (1955).
38. M. Kakudo and T. Watase, *Technol. Reports Osaka University*, **50**, 2, 247 (1952).
39. J. D. Bunning, J. W. Goodby, G. W. Gray, and J. E. Lydon, Proceedings of the European Conference, Garmisch-Partenkirchen, January, 1980, to be published.
40. J. D. Bunning, J. E. Lydon, C. Eaborn, P. M. Jackson, J. W. Goodby, and G. W. Gray, to be published.