

Forschung, Wissenschaft



7. Internationales Farbensymposium

Vom 24. bis zum 27. September 1979 veranstaltete der Schweizerische Chemiker-Verband unter dem Patronat der Schweizerischen Chemischen Gesellschaft und der Basler Farbenfabriken das 7. Internationale Farbensymposium in Interlaken (Schweiz).

Eine zusammenfassende Übersicht über die 28 gebotenen kurzen Mitteilungen erschien im November-Heft der CHIMIA (33 [1979] 429–431). 6 der 7 gehaltenen Übersichtsreferate werden in extenso in CHIMIA abgedruckt. Zwei Referate sind bereits im Januar-Heft erschienen (C. F. Bernasconi, CHIMIA 34 [1980] 1–11 und E. V. Dehmlow, CHIMIA 34 [1980] 12–20). Das vorliegende Heft bringt das Referat von G. W. Gray. Drei weitere Referate werden folgen.

Dyestuffs and Liquid Crystals*

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Abstract:

This review paper surveys the various modes whereby *electro-optical displays* using *liquid crystals* may be operated, and concentrates attention upon those displays in which *dichroic dyes* can be incorporated advantageously in the liquid crystal. The problems of finding dyes with suitable *order parameters*, *solubilities*, and *photochemical stabilities* are discussed in the context of extensive experimental work on *azo dyes* and *anthraquinone dyes*. Although very good displays can now be made using the best of such dyes, further research is needed before completely satisfactory dyes covering the yellow, the red and the blue colour ranges can be considered to be available.

Introduction

In recent years, liquid crystals have made a strong impact in the commercial world as a result of their application in electro-optical display devices [1], e.g. watches, desk calculators, instrument display panels, etc. The main reason for the success of these attractive liquid crystal displays lies in their extremely low power consumption, with a consequent long battery life for portable units.

One of the more recent developments in this field of work has been the use of dichroic dyes which are dis-

solved in the liquid crystal and provide a means of imparting colour contrast, as distinct from black and white contrast, to the display.

This article sets out to describe the current state of the art in relation to dye-liquid crystal displays.

a) Liquid Crystals

Organic solids which are composed of long, fairly rigid (rod-like) molecules frequently form a liquid crystal phase on being heated. This phase may then persist for a few degrees or for many tens of degrees before, at a higher temperature, the amorphous isotropic liquid is produced [2].

The reason for this behaviour is that even after the primary forces maintaining the order of the crystal lattice have been weakened by thermal effects, the rod-like molecules are able to retain a high degree of long range parallel order. Thus a fluid, but still extensively organised state or phase is produced, and so it becomes clear why such anisotropic fluids or ordered fluids have commonly become known as liquid crystals. The liquid crystal phases which may be produced from the solid crystal on heating may be of different types.

1) Smectic liquid crystals

Here the molecules lie parallel to one another with their ends in line, forming layers. The situation is akin

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to a layer crystal lattice except that, depending on the system, viscous flow is possible. This occurs with varying degrees of ease and involves the shear flow of layers or multiples of layers over one another.

The simplest form of the smectic phase is the smectic A phase in which the molecular centres of gravity within a given layer plane are disorganised, and on average the molecules are arranged with their long axes orthogonal to the layer planes. Some ten other polymorphic modifications of smectic phases are now recognised [3], but since these quite viscous and highly organised liquid crystal states are not of central importance to this article, we do not need to consider smectic liquid crystals any further here.

2) Nematic liquid crystals

These are formed either directly from a solid crystal or from a precursor smectic phase by heating. No layer arrangement is involved, and only a statistically parallel orientation of the long molecules persists in the highly fluid phase. The nematic order is illustrated in Fig. 1a. On heating to a higher temperature, the nematic phase passes to the isotropic liquid (Fig. 1b).

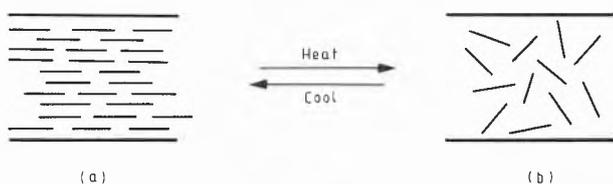
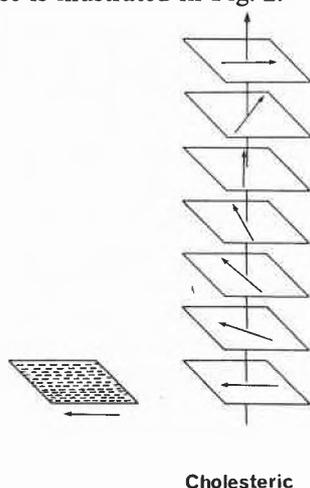


Fig. 1: Order-disorder situation at the nematic (a) to isotropic liquid (b) transition.

3) Cholesteric liquid crystals

When the compound consisting of rod-like molecules is optically active, a modified nematic phase called a cholesteric liquid crystal or a chiral nematic is formed on heating either the crystal or the precursor smectic phase.

A simple model to describe the molecular arrangement in this phase is illustrated in Fig. 2.



Cholesteric

Fig. 2: A simple model for the molecular order in the cholesteric liquid crystal phase.

The structure can be envisaged as a stack of sheets. In each sheet, the order is the same as in a nematic liquid crystal, but on passing from sheet to sheet, the long axes of the molecules are progressively displaced through a small angle. For a given cholesteric system, this angle is always in a clockwise or an anticlockwise direction, dependent upon the rotatory sense for the chiral compound under observation. As a result, a helix (a twisted structure) is built up. The director for this phase is the helix axis, whereas for the nematic, the director, is the average direction of orientation of the long molecular axes at a given location in the phase. The cholesteric phase is still quite fluid, but considerably more viscous than a nematic.

This simple model explains many of the unique optical properties of cholesteric liquid crystals. For example, their enormously high optical rotatory power compared with that of ordinary chiral, organic, isotropic liquids is explained by the supramolecular helix of the structure. Also, if the pitch of the helix (P) is such that the product of P and the refractive index (n) corresponds to a wavelength in the visible range of the

$$\lambda = Pn$$

(Equation 1)

spectrum, then the selective Bragg-type reflection from the series of sheets will lead to the reflection of coloured light from the phase. The wavelength and colour of this light will moreover be temperature dependent, since the pitch of the helix will respond by changing with temperature.

The cholesteric phase is therefore a twisted version of the nematic phase, and this explains why, (i) the addition of a chiral solute to a nematic produces a long pitch cholesteric, and (ii) the admixture of equal amounts of two cholesteric phases formed from enantiomeric pairs of materials produces a nematic liquid crystal.

The cholesteric phase again passes direct to the isotropic liquid on being heated to some higher temperature.

However, it is not always necessary to heat a crystal before a nematic or cholesteric phase is produced. In an increasing number of cases pure compounds or eutectic mixtures of pure compounds are being discovered which exist as liquid crystals in the ambient temperature range [4]. That is, the crystal is formed only on cooling the liquid crystal below room temperature, and the resulting solid re-melts to the liquid crystal at a temperature below ambient. The work of organic chemists in producing highly pure room temperature liquid crystal materials which have excellent thermal, photochemical and electrochemical stabilities has indeed been the single, most important contributory factor to the escalation in commercial impact which liquid crystals have made in the last few years. Some examples of materials which give rise to wide range nematic mixtures are given in Table 1.

Table 1: Examples of nematogens from which mixtures with wide nematic ranges may be derived

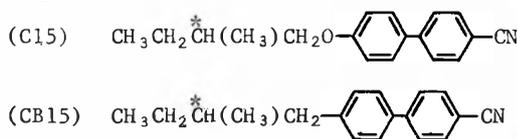
Compound Type	Comment	
$\text{Alky10}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{Alky1}$	Schiff's bases; rather unstable; yellow	
$\text{Alky10}-\text{C}_6\text{H}_4-\text{N}(\text{O})-\text{C}_6\text{H}_4-\text{Alky1}'$	Azoxy compounds; better stability, but not to U-V; yellow	
$\text{Alky10}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ $\text{Alky1}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ $\text{Alky1}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	Biphenyls and <i>p</i> -terphenyls; excellent stability; colourless	
$\text{trans-Alky1}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ $\text{trans-Alky1}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$		Phenylcyclohexanes (PCH's) and Biphenylcyclohexanes (BiCH's); excellent stability; colourless

Examples of commercial mixtures belonging to the last two categories are:

Biphenyls/ E 7 C, -10° ; N, 60.5° ; I
p-terphenyls [4]: E 37 C, -9° ; N, 89° ; I
 Supplier: BDH Chemicals Limited, Poole, Dorset, England

PCH's/ ZLI 1291 C, -10° ; N, 107° ; I
 BiCH's [5]: ZLI 1253 C, -5° ; N, 67° ; I
 Supplier: E. Merck, Darmstadt, West Germany

The addition of a chiral 4-alkyloxy- or 4-alkyl-4'-cyano-biphenyl (see below) to any of the above commercial mixtures gives a cholesteric liquid crystal of pitch determined by the concentration of the chiral dopant.



e.g. 3% w/w CB15 in E7 gives
 C, -10° ; Ch, 55° ; I; Pitch = $3\ \mu\text{m}$

b) Electro-optical Displays

A liquid crystal, electro-optical display consists of a thin film of liquid crystal (6–20 μm thick) contained between two glass plates whose inner surfaces carry a transparent coating of SnO_2 or In_2O_3 to function as electrodes and allow an electric field to be put across

the film. By suitable treatments* of the electrode surfaces it is possible to control the alignment of the director in the liquid crystal so that in a nematic, for example, this lies either parallel to the electrode surfaces (homogeneous alignment) or orthogonal to the electrode surfaces (homeotropic alignment) and extends right through the thin film, giving a transparent "single crystal" or monodomain sample—see Fig. 3.

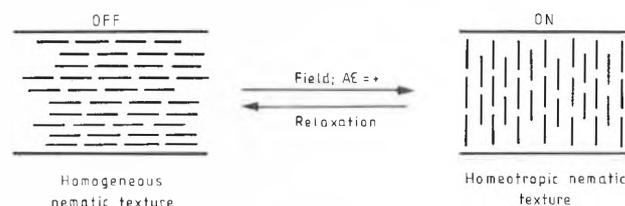


Fig. 3: Homogeneous (left) and homeotropic (right) alignments of a nematic liquid crystal film and one *Fréedericksz* mode of operating a liquid crystal display.

With reference to Fig. 3, let us now assume that the molecules represented by the lines are of positive dielectric anisotropy**. Application of a field will

* For example: (i) unidirectional rubbing with tissue, (ii) deposition of a thin film of polyvinyl alcohol and unidirectional rubbing with tissue, (iii) deposition of a thin film of a lipid such as lecithin, (iv) oblique evaporation of SiO (SiO_2/Si). Techniques (i) and (ii) give homogeneous alignment, technique (iii) gives homeotropic alignment, and technique (iv) gives homogeneous alignment at tilt angles from 0° to 25° determined by the angle of oblique evaporation.

** This situation obtains when the permittivity along the long axis of the molecule (ϵ_{\parallel}) is greater than ϵ_{\perp} , i.e. $\epsilon_{\parallel} - \epsilon_{\perp} = +ve$. This occurs when the molecule has a strong terminal dipole lying along the long axis, e.g. in molecules carrying a terminal cyano group.

now turn the molecules away from a homogeneous alignment, as in Fig. 3 (left), and give a homeotropic alignment.

If the cells are contained between suitably oriented sheets of polariser, this electrically induced change in molecular orientation will dramatically change the optical characteristics of the film from birefringent and bright to black. On switching off the field, the nematic will relax back to the homogeneous alignment under the influence of a thin film of molecules (at the electrode surfaces) which maintain the homogeneous alignment even in the on state. Thus, an electro-optical shutter has been created.

It is now obvious that with a liquid crystal of negative dielectric anisotropy we could electrically switch the homeotropic alignment on the right of Fig. 3 to the homogeneous alignment on the left.

This describes the *Fréedericksz mode* of operation of a device, and again it is obvious that if parts of the display area can be selected for electrical stimulation, then we have a means of displaying information at will; e.g. letters, numbers, diagrams, etc.

The display mode which has proved itself to be most successful in commercial devices has however been the *Twisted Nematic mode*. It is not necessary to elaborate here upon the detail of its operation except to say that the thin film of nematic again has the homogeneous alignment, but the direction of alignment (the director) at the two electrodes is at right angles. The director therefore rotates through 90° across the thickness of the film which therefore has a quarter helical structure. The cell is again contained between crossed polarisers, the liquid crystal must be of positive $\Delta\epsilon$, and the field switches the alignment to homeotropic. Black information on a bright background or bright information on a black background can be displayed dependent upon the mutual orientation of the external polarisers; contrast is excellent. Rise and decay times of < 100 ms at operating voltages in the 1.5 to 2 V range, with power consumption in the μ watt range, can be readily achieved.

A disadvantage of these devices lies however in the need to use polarisers*, and from this standpoint, the Cholesteric-nematic Phase Change display has attractions. For this display mode, we require a fairly long pitch cholesteric (e.g. $4-5 \mu\text{m}$) of positive dielectric anisotropy. As in the other two cases, we are concerned with generating a field effect between conductively coated plates, and so the liquid crystal must be of high resistivity. As illustrated in Fig. 4 (A), the off-state of the cell involves a random arrangement of helical domains. This is the so-called focal-conic texture of the cholesteric phase, and it scatters light. On appli-

cation of a field, the helices gradually tip over and become more nearly parallel to the supporting plates. When a sufficiently large field is applied, the helices effectively unwind as the molecules of positive $\Delta\epsilon$ align with their long axes parallel to the field. A homeotropic nematic alignment which is clear is therefore produced. Since we have gone from a scattering to a clear state, an electro-optical effect has been achieved *without* the use of polarisers. However, the contrast is not good, unless thick films are used, and when this is the case the threshold field is high.

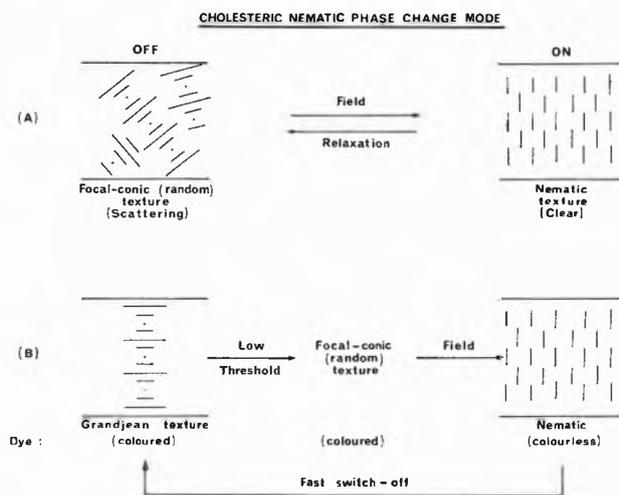


Fig. 4: Modes of operating the cholesteric-nematic phase change display and the effect of added dichroic dyes.

To overcome the poor contrast and permit the use of thinner films which can be operated at reasonably low fields, White and Taylor [6] first conceived the idea of dissolving a dichroic dye in the cholesteric liquid crystal. As illustrated in Fig. 4 (B), we commence in the off-state with the Grandjean texture. The molecules are aligned homogeneously at the electrode surfaces, and the helical axis is orthogonal to the plates. A dichroic dye consisting of elongated molecules is dissolved in the cholesteric. The dye molecules tend to align parallel to the host molecules of the cholesteric solvent, and therefore the incident unpolarised light will always have some component vector along the long axis of the dye molecule. The display will therefore be strongly coloured with the colour of the dye used. On application of a field, the helices first tip over at low threshold to give the focal-conic texture [the starting state in Fig. 4 (A)] which is also coloured. Eventually, as before, the homeotropic nematic texture is formed at a high enough field, and in this state the dye molecules are aligned perpendicular to the electrodes and parallel to the direction of propagation of the light. The cell is now colourless or very weakly coloured, and so a good contrast has been achieved without the use of polarisers.

On switching off, the chiral molecules regenerate the helical situation by random nucleation, and if fast

* Polariser sheet leads to a loss in light intensity both for the reflective and the transmissive mode of operation. Also the polariser sheet is an expensive component which is difficult to affix externally to the cell.

switch off is used, the original *Grandjean* texture is restored.

The dye phase change display can therefore be operated from either the focal-conic or *Grandjean* textures and the parameters affecting [7] the electrically induced effect are:

$$E_c P = \pi^2 \sqrt{\frac{k_{22}}{\epsilon_0 \epsilon_a}} \quad (\text{Equn 2})$$

where E_c = the critical field, P = the helical pitch, ϵ_a is the dielectric anisotropy, ϵ_0 is the permittivity of free space, and k_{22} is the twist elastic constant.

With strongly absorbing dyes which have a suitably high solubility in the liquid crystal host, good contrast can now be achieved (e.g. 10:1) in cells which are only 12 μm thick and have a threshold voltage of around 5 V; moreover the viewing angles of the displays are excellent ($\sim \pm 80^\circ$).

The quality of the device is of course determined by a number of factors and very important amongst these is the nature of the dye which is used. Before we go on to consider this aspect it should however be pointed out that features of cell design are also quite critical. For example, it is found that a surface treatment which induces the molecules to stand up at right angles very near to the electrode can be advantageous. The molecular arrangement in the cell is now as shown in Fig. 5; the changes which occur with increasing field are exactly as described in Fig. 4 (B). However, the on state of the cell is now uniformly clear, whereas with the homogeneous alignment [Fig. 4 (B)], a fuzzy or patchy on state is produced. This is probably caused by the residual, variable absorption arising from dye molecules trapped parallel to the surface in the few layers of cholesterogen molecules which retain the homogeneous alignment in the on state. With the arrangement in Fig. 5, the homeotropic alignment retained in the surface layers favours the nematic arrangement, and with decreasing field, the uniform colourless state persists until low values of V and the optically active state (Fig. 5) is regenerated spontaneously.

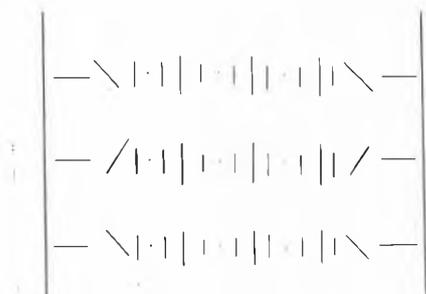


Fig. 5: Initial state of alignment of a cholesteric-nematic phase change display with a homeotropic alignment close to the surface; ϵ_a is again positive.

It will be realised that the cholesteric-nematic phase change modes involving dyes that have been described

so far will give a negative contrast display, i.e. the activated areas are colourless against a coloured background. It is however possible to produce a positive contrast display, i.e. coloured information on a colourless background. The cholesteric liquid crystal must now be of *negative* dielectric anisotropy, and of long pitch (ca. 8 μm). The surfaces are treated with lecithin to induce the molecules to stand up orthogonal to the surfaces. Indeed, the surface forces are sufficiently strong to unwind the fairly long helices (at least to a very large extent), so that effectively, the off state of the cell is a homeotropic nematic as on the right of Fig. 3 or of Fig. 4 (A) or (B). Application of a field now turns the molecules round so that they lie parallel to the surfaces. Surface forces no longer control the situation, the helices reform, and the on state of the cell is now the *Grandjean* texture shown on the left of Fig. 4 (B). Therefore, with added dichroic dye, the off state is colourless and the on state is coloured, giving the necessary positive contrast. It seems likely that this display mode will become very important, but not until better negative cholesteric materials are available; progress in this direction is already being made.

However, the primary factors concerning quality of device relate to the dyes which are used. Let us now consider this important aspect.

Dyes for cholesteric-nematic phase change displays

The use of pleochroic dyes as additives to liquid crystals was first suggested by *Heilmeyer* and *Zanoni* [8] in 1968. The contrast ratio of their device, based on a *Fréedericksz* type cell was however poor, and the cell required one external polariser, giving poor brightness. Since the work of *White* and *Taylor* [6] pioneering the use of dyes in phase change devices which require no external polarisers, this form of device has attracted most attention, and we will concentrate on it. However, *Uchida*, *Shishido*, *Seki* and *Wada* [9] have investigated alternative dye-liquid crystal display modes (i) using a twisted nematic state and (ii) using a slightly pretilted homeotropic nematic of negative dielectric anisotropy—i.e. a *Fréedericksz* type cell. Both (i) and (ii) require an external polariser, but (ii) does again have the advantage that the on areas are coloured, giving a positive display pattern, as distinct from the colourless-on-coloured display of some phase change devices. However, space does not permit further discussion of these interesting alternatives.

a) Dye Requirements

Enormous numbers of dyes are commercially available, but only a few are useful in liquid crystal displays. The dyes must be non-ionic since high resistivities must be maintained in devices operating by a field effect. The dyes must also be highly pure (not a regular feature in many commercial dye products) and they must be soluble in (compatible with) the liquid crystal; this limits

the dyes to those of the disperse type, and azo dyes seemed particularly attractive.

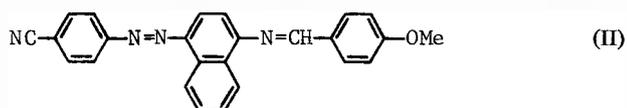
One of the first dyes examined by *Heilmeyer* and *Zannoni* [8] was Indophenol Blue (I)



but this did not give a satisfactory contrast or brightness. Even if the dye molecules only absorb light polarised along their long axis, light polarised perpendicular to the director of the liquid crystal will still be absorbed to some extent if the long axes of the dye and liquid crystal molecules are imperfectly aligned. A relatively short and fairly broad dye such as (I) was not therefore a very suitable choice.

A further problem is that the pleochroic character of the dye depends on the orientation of the transition moment of the dye with respect to the electric vector of the incident light. The ideal situation will therefore arise only if the long axis of the dye molecule is coincident with the direction of orientation of the transition moment. Otherwise the long axes of the dye molecules will orientate with the liquid crystal director, which will then not be aligned with the direction of the transition moment.

From this standpoint again, azo dyes seem attractive and for the dye (II), for example, *White* and *Taylor* [6]



report an order parameter* of 0.77 in a *Schiff's* base nematic mixture. This raises two points of interest. First, the improved performance of dye (II) over dye (I) shows how the broadening effect of the naphthalene ring is compensated for by the extended length of dye (II). Secondly, the order parameter of 0.77 is greater than that (0.60) of the nematic host alone. This is not unreasonable because the dye molecules (II) are longer than the host nematic molecules and less subject therefore to thermal fluctuations. Also, like reinforcing rods in concrete, the longer dye molecules may lead to increased local order in the nematic.

b) Measurement of Dye Order Parameter

The order parameter S of dyes dissolved in nematic liquid crystals are obtained [10] from the absorbance A ($= -\lg$ [transmission]) of light polarised parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the director of parallel, homogeneously aligned films using the expression

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

* Ordinary parameter = $S = 1$ for a perfectly aligned nematic;
 $S = 0$ for an isotropic liquid

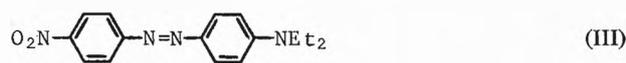
Absorbances are measured spectrophotometrically, and the zero line ($A = 0$) is determined using a control nematic film without dye. Nematic films are generally $12 \mu\text{m}$ thick and aligned homogeneously on a rubbed polyvinyl alcohol coating. Dye concentrations are varied around 0.5% by weight, but in order to determine S accurately the important point is to use dye concentrations and film thicknesses such that $1.0 < A_{\parallel} < 2.0$ and $A_{\perp} > 0.10$. High grade polaroid (HN 32) should always be used.

Although divergence of the direction of the transition moment of the dye and the nematic director is a problem in some cases, generally speaking the S value for a dye provides a good figure of merit for the performance of a given dye in dye phase change displays.

It should be noted that for a given dye, the S value depends on the host nematic used. *Jones* and *Reeve* [11] have observed some inversion of order parameters when the nature of the host is changed considerably. For example, S values for anthraquinone dyes were found to increase in E7* compared with a *Schiff's* base host, whereas azo dyes showed a marked increase in S in the same *Schiff's* base host compared with E7. Even when the chemical nature of the host is kept approximately the same by changing from E3* to E7 to E8* and E9*, significant increases in S values are observed (Table 2).

The increases in S follow the increases in the host clearing temperature as the content of 4-alkyl-4'-cyano-*p*-terphenyl is raised. It would seem reasonable that this should be so, as the measurements (carried out at room temperature) are being made at temperatures progressively further away from the clearing point as we go from E3 to E9, i.e. nematic hosts (with increasing order parameters) which are more ordered at room temperature are being used.

It should also be noted here that with solvents such as E3, E7, E8 and E9, which are strongly dipolar due to the presence of the cyano groups, bathochromic shifts in λ_{max} are observed relative to the λ_{max} values in non-polar solvents. For example, *Jones* and *Reeve* [11] observed a λ_{max} for dye (III) of 510 nm using E7, compared with λ_{max} values of 501 using



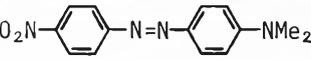
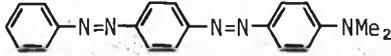
N,N-dimethylformamide, 483 nm using ethanol, and 479 nm using benzene as solvent.

c) Results on Azo Dyes

The S values for the azo dyes in Table 2, particularly the increase in S obtained with the change from a mono

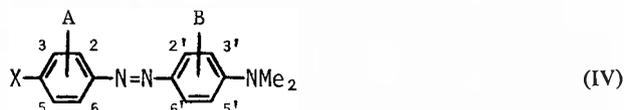
* E3, E7, E8 and E9 are commercial mixtures (supplied by BDH Chemicals Limited, Poole, Dorset) of 4-alkyl- and 4-alkoxy-4'-cyanobiphenyls, E7, E8 and E9 containing some of a 4-alkyl-4'-cyano-*p*-terphenyl.

Table 2: Order parameters (*S*) for two dyes in chemically similar hosts with increasing clearing points (N-I)

Host Data	HOST			
	E3	E7	E8	E9
Clearing point (°C)	55	60.5	70.5	82
DYE				
	0.60	0.70	0.70	0.71
	0.67	0.74	0.75	0.78

to a bis azo dye, encouraged some detailed investigations of azo dyes to be made. Separate investigations were made by my own group at Hull University and by Jones and Reeve at Leeds University, at about the same period of time, and the following data are representative of the results obtained in both laboratories. Our general aim was to prepare dyes of high order parameter to give a black to white phase change display. To obtain black, all spectral colours must be absorbed, and this can be done by mixing yellow, red and blue dyes. Blue dyes are the most difficult to obtain due to the low electronic energy transitions required in the molecule so that they absorb red light, thus appearing blue. Red and yellow dyes are therefore easier to obtain.

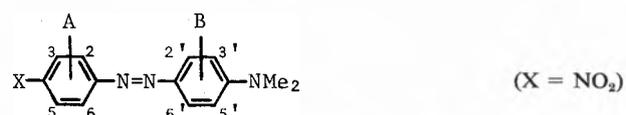
Considering the system



the effect of the electron withdrawing end group X on colour was that a shift to blue occurred in the order



When X = H, and there are no A or B substituents, *S* is only 0.48 in E7, and for X = CN and NO₂ similar *S* values of about 0.60 were obtained. Therefore to obtain high *S* values for strongly blue dyes, we concentrated on dyes with terminal NO₂ groups as X.

Table 3: Effects of lateral substitution on λ_{max} and *S* for some azo dyes

Substituent A	Substituent B	Shift in λ_{max} (nm)*	<i>S</i> (E3)
H	H	—	0.57
2-Cl	H	~20	0.56
2-NO ₂	H	~40	0.44
2,6-Di-Cl	H	-32	0.43
2,5-Di-Cl	H	v small	0.50
H	2'-Me	~10	0.50
H	3'-Me	-40	0.37

* A positive value represents a change in dye colour towards blue

The effects of lateral substituents A and/or B were then investigated. The situation is summarised in Table 3. Any lateral substitution therefore causes a drop in *S* value, but the most effective shifts in dye colour to blue are achieved by a 2-NO₂ or a 2'-methyl group. The dye (IV) with X = NO₂, a 2-NO₂ and a 2'-Me group has a λ_{max} of 560 nm (blue shift = 52 nm) and *S* = 0.45, i.e. the 2'-Me group gives no additional fall in *S* value within experimental error. The best colour that can be achieved with mono-azo dyes is therefore purple. Replacement of one or other of the two benzene rings in (IV) by 1,4-disubstituted naphthalene rings does give a significant colour shift to blue, but large decreases in *S* also occur.

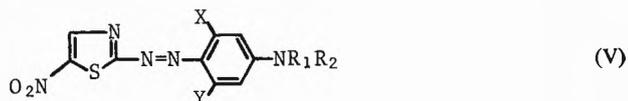
Even bearing in mind that the *S* values in Table 3 are for E3, and that higher order parameters would be obtained with hosts such as E7 and E8, it was obvious that mono-azo dyes of these types would not yield high enough order parameters with sufficiently strong blue colours.

Our interests therefore moved on to bis- and tris-azo dyes, but before considering these systems, a further brief comment on the mono-azo dyes of type (IV) should be made. The shifts in λ_{max} in Table 3 can be accounted for fairly consistently in terms of the electron supply and withdrawal situation in the molecules, together with considerations of steric effects either twisting the molecule such that the two rings cannot be coplanar, or twisting the -NMe₂ group out of the plane of the molecule. Jones and Reeve [11] went on to consider a much wider range of mono-azo dyes of the general type (IV), and from their extensive results, have observed a consistent quantitative effect of substituent groups, both terminal and lateral, on order parameter relative to that (*S*₀) of the parent 'dye', where A=B=X=H and NMe₂ is replaced by H. From their results, incremental ΔS values for given changes of substituent are obtained, and taking into account the number and position of the substituents in their summation, it is possible to calculate an order parameter for a particular system. A linear equation of the form

$$S_{\text{calc}} = S_0 + \sum \Delta S \quad (\text{Equn 3})$$

can therefore be applied. The agreement between observed and calculated *S* values is very striking indeed,

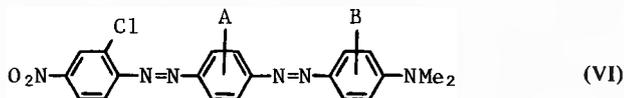
and it has been shown that the equation can be extended to 5-nitrothiazole dyes of structure (V)



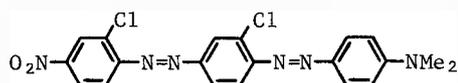
These dyes were of particular interest because the red shift in λ_{\max} is up to 105 nm compared with the analogous phenyl azo dye, and this means that the dyes are much more blue. Although electronic excitation of the polarisation band is achieved more easily, there is no attendant increase in S . For dye (V) with $X=Y=H$ and $R_1=R_2=Me$, S in E7 is 0.56.

Three-ring dyes

Using 3-chloro-4-nitrosonitrobenzene, several three-ring dyes of the general structure (VI) were prepared, and, as with all dyes tested [12], rigorously purified by column chromatography on alumina.



The dyes varied in colour from red to purple and had order parameters which were usually > 0.64 in E3, e.g. for



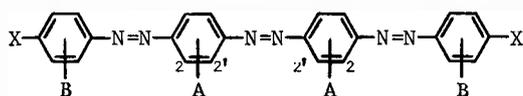
$\lambda_{\max} = 560$ nm; $S = 0.65$ in E3 and 0.74 in E8

Four-ring dyes

Unsymmetrical four-ring dyes have proved very difficult to make and/or purify; the products are very insoluble and consequently difficult to handle.

Symmetrical azo dyes

Our attention then turned to so-called symmetrical dyes of the type



These are fairly readily obtained by a reductive coupling of the nitro compounds corresponding to the two halves. The solubilities of such dyes with $X = NMe_2$ or OAlkyl were in the range 0.5–0.04 wt %; three-ring unsymmetrical dyes have solubilities in the upper end of this range. However, the four-ring symmetrical dyes appear to give more intensely coloured solutions at their solubility limit. By comparison, simple mono-azo dyes of type (IV) have solubilities in E7 which usually lie between 0.4 and 2.2 wt %.

The four-ring symmetrical dyes have colours ranging

from orange ($X = OAlkyl$) to purple ($X = NMe_2$) and S values > 0.65 are normal. For example for $X = NMe_2$, $B = H$ and $A = 2-Cl$, $\lambda_{\max} = 570$ nm and $S = 0.71$ in E3 and 0.75 in E8.

Attempts to obtain pure three-ring symmetrical azo dyes were not successful, and the preparation of one five-ring azo dye of a symmetrical nature yielded a product which was so insoluble that any form of analysis proved to be inconclusive.

So far this work had yielded orange, red, and purple dyes with S values upto 0.75 in E8, and although still higher S values might have been achieved, it seemed likely that low solubility would negate their value. We therefore changed our tactics to use a better electron donor system than NMe_2 and/or a better electron acceptor system than p -nitrophenyl, in an attempt to push the dye colour more into the blue region.

5-Nitrothiazole and julolidine dyes

In an attempt to obtain further red shifts in λ_{\max} , a range of 5-nitrothiazole dyes and julolidine dyes was investigated [10, 12]. The former dyes did provide blue materials, but the latter were at best purple-blue in colour. In the early stages of testing these dyes, however, their very considerable sensitivity to ultra-violet light became obvious. This is clearly a deficiency in any material to be used in an electro-optical display device. Although the dye is quite effectively protected between the containing glass plates of the cell, and indeed a phase change device incorporating the julolidine dye shown in Table 4 has been operational, exposed to ordinary light, without visible depreciation for over two years, the light sensitivity of these dyes was considered too serious a disadvantage from a commercial consumer standpoint to justify continuation of the programme. The results in Table 4 summarise the situation and show that although the investigation of azo dyes had provided many good, high order parameter dyes (up to 0.80 in E9), only the orange and red dyes could be judged to have an acceptable UV stability for commercial purposes.

Very full studies by Jones and Reeve [11] of the light fastness of dyes in liquid crystal media have been made. Their results are more detailed than ours, and confirm the considerable light sensitivity of 5-nitrothiazole and julolidine dyes.

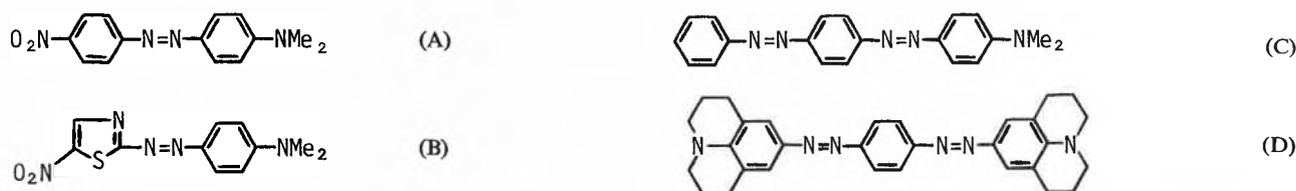
The nature of the work was now switched to dyes which would have a higher ultra-violet stability, and attention was immediately centred on anthraquinone type dyes.

Anthraquinone dyes

Although anthraquinone dyes seem structurally to depart rather widely from the basic concept of a rod-like molecule which will be compatible with a liquid crystal host, their reputed light fastness was an attractive feature. As will be seen, despite their molecular shape, remarkably good S values have been observed.

These studies of anthraquinone dyes now reported have

Table 4: Results for some azo dyes relevant to their use in electro-optical displays



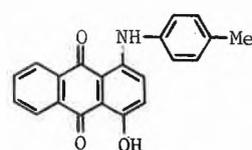
Dye	λ_{\max} (nm) and colour in E8 at 20°	Order parameter and solubility in E8 at 20° (wt %) (in brackets)	Absorbance in E8 at λ_{\max} at 20° (12 μ m layer)	Effect of UV light ** for 15 min	Life-time of display in hours
(A)	508 ORANGE-RED	0.70 (0.4)	1.4	Almost none	> 15,500
(B)	594 BLUE	0.70 (0.4)	1.3	Considerable bleaching	4,000
(C)	505 ORANGE	0.75 (1.3)	1.8	None	> 15,500
(D)	568 PURPLE	0.79* (1.0)	4.0	Considerable bleaching	2,000

* S in E9 = 0.80

** A 150 W high pressure mercury light was focused by a silica lens down to a 2 mm spot. The liquid crystal film was 75 μ m thick and enclosed by silica plates. Temp rise during exposure occurred—up to 35°.

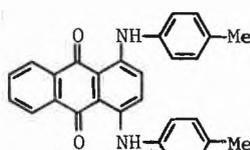
been conducted entirely at the Laboratories of BDH Chemicals Limited at *Poole* [13] but again *Jones* and *Reeve* at Leeds have carried out complimentary studies which have led to similar conclusions.

The first promise of useful properties came from an examination of commercial Thermoplast Blue P (VII).



(VII)

λ_{\max} in E7 = 595 nm;
 S = 0.615

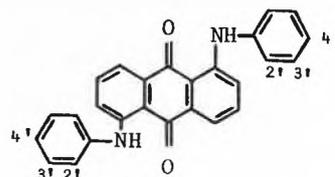


(VIII)

The 1,4-disubstituted analogue (VIII) is green and gives a much lower S value.

Modifications to the structure of dye (VII) were now made. Replacement of the 1-*p*-toluidino-group by an alkylamino group gave lower S values, and movement of the substituent in a 1-*p*-substituted anilino group from the *p*- to the *m*- to the *o*-position gave a decrease in S -value. Lengthening of the alkyl group in the 1-*p*-alkylanilino group also decreased S , but lengthening in the chain of a 1-*p*-alkoxyanilino group increased S , such that the highest S value of 0.65 was achieved in E7 with a 1-*p*-*n*-nonyloxyanilino grouping (dye D 16)— λ_{\max} = 596 in E7. With a 1-*p*-dimethylamino group (dye D 27), the value in E7 was 0.63, and λ_{\max} was 612.

1,5-Antraquinone dyes were now examined to increase the length of the dye molecule. The resulting dyes have the structure (IX).



(IX)

Dye (IX) itself is purple, and in E7 gives an S value of 0.58; λ_{\max} = 544 nm. The S value of dye (IX) was improved by incorporation of a 4'-substituent in each ring, and the S values for the 4'-alkyl compounds were slightly lower than those for the best members of the 4'-alkoxy series. Movement of the 4'-substituents to the 3'- and 2'-positions or replacing the alkylanilino groupings by alkylamino groupings gave lower S values.

Also 4'-alkyl-substituted compounds absorbed at higher λ_{\max} values than 3'- or 2'-, whilst 4'- and 2'-alkoxy compounds absorbed at similar wavelengths and approximately 5 nm higher than their 3'-substituted analogues.

The results in Table 5 are taken from a recently presented paper by *Constant, Pellatt and Roe* [13].

The data in Table 5 show that order parameters of about 0.69 were achieved. Though not as good as the highest S values for azo dyes, these values still permit the production of display devices with eminently satisfactory contrast. The 4'-dimethylamino compound

Table 5: Results for λ_{\max} and order parameter for some 1,5,4'-substituted anilinoanthraquinones of structure (IX)

Dye no	4'-Substituent	λ_{\max} in E7 nm	Order Parameter in E7
D33	None	544	0.58
D34	Methyl	555	0.65
D35	Ethyl	554	0.67
D36	<i>n</i> -Propyl	556	0.65
D37	<i>n</i> -Butyl	556	0.66
D38	<i>n</i> -Pentyl	555	0.63
D67	Hydroxy	524	0.59
D39	Methoxy	555	0.67
D40	Ethoxy	555	0.65
D41	<i>n</i> -Propoxy	555	0.625
D42	<i>n</i> -Butoxy	556	0.66
D43	<i>n</i> -Pentoxy	557	0.68
D44	<i>n</i> -Hexoxy	556	0.69
D45	<i>n</i> -Heptoxy	557	0.69
D46	<i>n</i> -Octoxy	556	0.69
D47	<i>n</i> -Nonoxy	556	0.68
D48	<i>n</i> -Decoxy	556	0.67
D52	Dimethylamino	546	0.65
D53	Morpholino	542	0.65
D54	Phenylazo	524	0.71
D66	Phenyloxy	554	0.67
D76	N-ethyl-N-2-hydroxyethyl	551	0.62
D77	Isopropyl	558	0.68

(dye D52) is also attractive because of its broad absorption band.

Dye solubility is of course very important, and this is very variable over the dyes of types (VII) and (IX). Generally speaking, an absorbance of at least 1.0 in a 12 μm cell is required, and usually this was given by dyes with a solubility of 1.5 wt % or better. Some of the best solubilities for 1-4'-substituted arylamino-4-hydroxyanthraquinones (VII) and 1,5-disubstituted anthraquinones (IX) are:

Dye	Solubility (wt %)	Dye	Solubility (wt %)
D5	> 5	D37	> 5
D16	2.2	D77	1.6
D35	1.7		

The solubilities of many of the dyes therefore fall below the desired level, and this factor, coupled with the somewhat lower *S* values compared with azo dyes imposes some restrictions on their utility.

However, the property which makes the anthraquinone dyes very attractive relative to the azo dyes is their very high stability to ultra-violet irradiation.

The following studies by *Constant, Pellatt and Roe* [13] illustrate this stability. Samples of each dye were dissolved in E7 or E9, and cells containing the solution were exposed to low level UV light from a low power lamp (a General Electric F20T12BLB Black Light Fluorescent Lamp) or a strong UV light from a medium power lamp (Hanovia UVS 500 Arc Tube type 509/10 with quartz tube, total output 500 watts).

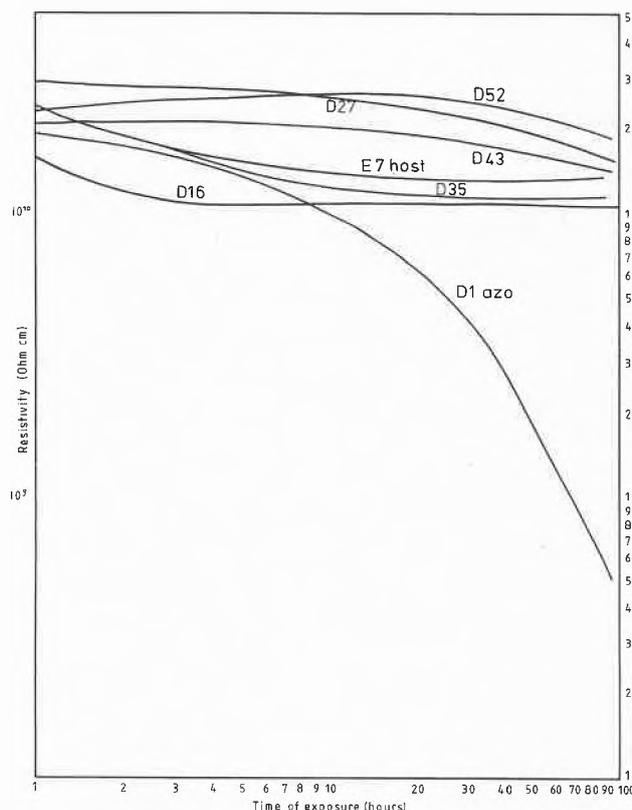


Fig. 6: Effect of UV irradiation on the resistivities of solutions of some anthraquinone and azo dyes in E7 or E9 (exposure up to 100 hours).

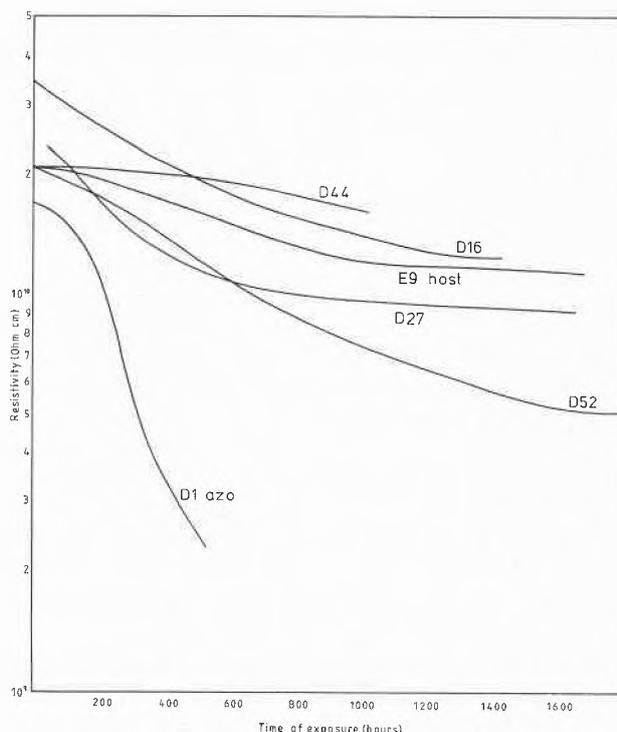


Fig. 7: Effect of UV irradiation on the resistivities of solutions of some anthraquinone and azo dyes in E7 or E9 (exposure up to 1800 hours).

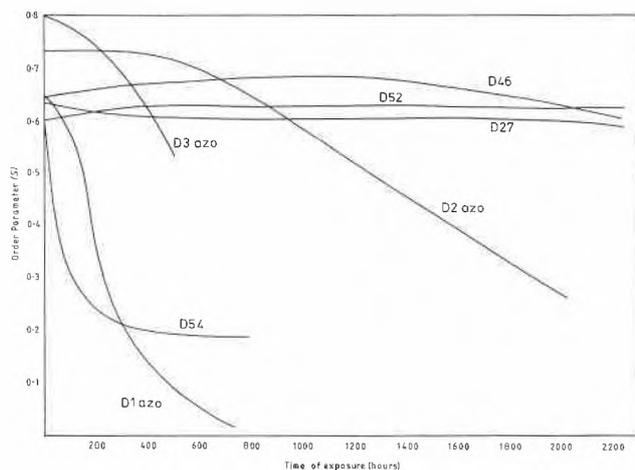


Fig. 8: Effect of UV irradiation on the order parameters of some anthraquinone and azo dyes dissolved in E7 or E9 (exposure up to 2200 hours).

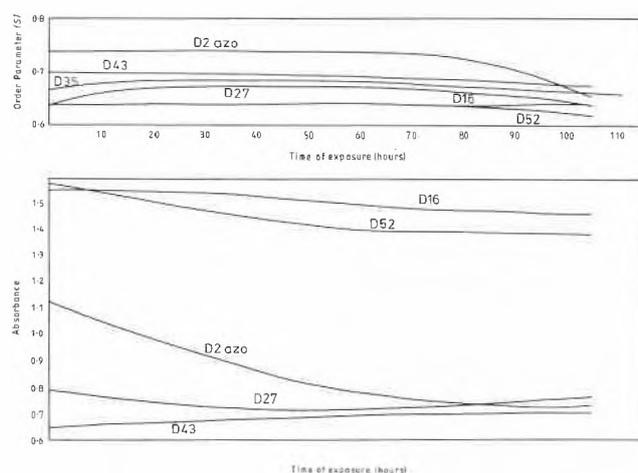


Fig. 9: Effect of UV irradiation on the order parameters of some anthraquinone and azo dyes dissolved in E7 or E9 and on the absorbances of the solutions (exposure up to 100–110 hours).

Control cells containing only the host nematic were used, and cells were placed on a heat sink plate 15 cm from the GE Black Lamp or 20 cm from the Hanovia lamp.

The effect of the irradiation was checked by monitoring the changes in (a) resistivity, (b) order parameter and (c) absorbance. Figs. 6 to 9 illustrate the results and show the high stability of dyes D16, 27, 43, 44, 46 and 52. Only dye D54 is poor (Fig. 8), and this is a 1,5-disubstituted anthraquinone carrying an azo linkage in each substituent. The behaviour of dyes D1 and D3—both azo dyes, shows the generally low stability of the azo type of dye; azo dye D2 (the bis-azo dye in Table 2) is however more satisfactory.

Conclusions

From these studies, it is clear that yellow-red azo dyes of very high order parameter and reasonable stability to UV can be made. Purple or blue azo dyes have good

S values, but low stability. Blue anthraquinone dyes of good order parameter and very high stability can however be made, only their solubility being a limiting factor (and to some extent their S-values).

The existing dyes of good to high order parameter therefore permit the construction of a high contrast, black and white dye phase change display using the best of the yellow-red azo dyes and the best blue anthraquinone dyes.

If however we are seeking a more perfect situation, it is obvious that more soluble blue dyes with higher S values, and more stable yellow-red dyes are desirable, and if this is to be achieved, more work certainly remains to be done. Reports of good properties for cyanine type dyes have been made [14], but in our experience, their solubilities and stabilities are too low.

Acknowledgments

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