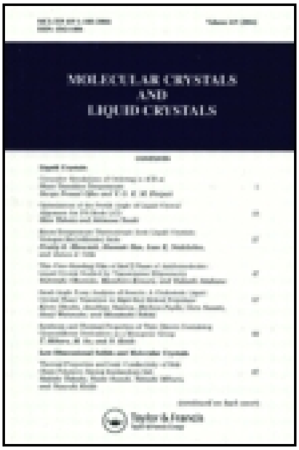

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Measurement of Phase Transition Temperatures in Liquid Crystals Using the Temperature-Dependent Dielectric Constant

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Version of record first published: 19 Dec 2006.

To cite this article: C. Somerton (1988): Measurement of Phase Transition Temperatures in Liquid Crystals Using the Temperature-Dependent Dielectric Constant, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 154:1, 77-87

To link to this article: http://dx.doi.org/10.1080/00268948808078724

Mol. Cryst. Liq. Cryst., 1988, Vol. 154, pp. 77–87
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Printed in the United States of America

Measurement of Phase Transition Temperatures in Liquid Crystals Using the Temperature-Dependent Dielectric Constant

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(*Received May 11, 1987*)

This work describes a technique for the accurate determination of phase transition temperatures in liquid crystals. It is based on the temperature-dependent dielectric constant (TDDC) which shows discontinuities at phase transitions. A plot of the dielectric constant differentiated with respect to temperature ($d\epsilon_r/dT$) versus temperature, exhibits peaks as the materials are heated or cooled through phase transitions. It has been shown that this technique easily detects transitions such as that from smectic A to smectic C, which other techniques have difficulty detecting.

The work is illustrated with two materials, and results from seven materials covering a wide variety of phase transitions are compared with values given by other techniques.

Keywords: phase transitions, dielectric constants

INTRODUCTION

It is widely known that the molecular structure of liquid crystals is dependent on temperature. There are certain ranges in which a particular molecular arrangement (or phase) exists, heat or cool it and the structure changes. Some structures lend themselves to practical applications, some do not, hence it is important to know the working temperature range of any liquid crystal based device.

The usual methods of determining phase transition temperatures involve recognition of changes of appearance of the sample using hot stage optical microscopy or detection of enthalpy changes using differential scanning calorimetry (DSC). Optical determinations are usually performed between crossed polars on a microscope fitted with a hot stage. Some phase transitions such as those from smectic A to hexatic B of *n*-hexyl-4-*n*-pentyloxybiphenyl-4-carboxylate (650BC),[1] the smectic I (schlieren) to smectic F (mosaic) and the focal conic fan textures of smectic I to smectic F in terephthalylidene-bis-4-*n*-decylaniline (TBDA)[1] involve only subtle changes of texture and require an experienced eye to detect them. Another complicating factor is that for a given material, the same phase can appear in totally different textures—for example the focal conic and polygonal textures of the smectic A phase of *n*-decyl 4-(4'phenylbenzylidene-amino) cinnamate.[1]

DSC easily detects phase transitions such as smectic A to nematic or isotrópic and transitions to and from smectic B which have large enthalpy changes. There are however some transitions such as nematic or smectic A to smectic C, and smectic F to smectic G where the enthalpy changes are small (<1 kJ mol^{-1}) and may go undetected even with the most sophisticated modern instruments. This work describes a simple alternative technique based on the change of dielectric constant at phase transitions.

This phenomenon has been known for some time and occurs in a wide range of compounds.[3] For example Carr[5] noted discontinuities in the dielectric loss (at microwave frequencies) for the phase transitions in ethyl-*p*-azoxybenzoate and Wirth and Wellman[6] used a dielectric constant technique to measure genotypic transitions in sodium palmitate. These transitions were termed crystal–subwaxy–waxy–superwaxy–subneat. The works reported in Reference 3 concern the dielectric anisotropy, dispersion and relaxation. Large changes in these properties at phase transitions were observed, although (to the author's knowledge) the effect does not seem to have been utilised as a method of determination of phase transition temperatures.

The way in which the dielectric constant is defined needs a brief comment. Due to the nature of liquid crystal molecules the dielectric constant parallel to the long molecular axis ($\epsilon_{\parallel}$) and perpendicular to the long molecular axis ($\epsilon_{\perp}$) are different, (giving rise to the dielectric anisotropy). In this work no attempt was made to align the molecules in any particular orientation, so the use of the term "dielectric constant" is rather loose and refers to some ill-defined average between $\epsilon_{\parallel}$ and $\epsilon_{\perp}$. However, in this application, this is of no consequence since it is changes in the dielectric constant (not its absolute value) which are detected.

EXPERIMENTAL

Experimental cells were constructed from 2 cm × 2 cm × 1 mm indium/tin oxide (ITO) coated glass cleaned and degreased by a well established method.[7] The ITO was etched off two parallel edges by standard photolithographic techniques[8] to produce a strip 1 cm wide down the middle of each plate. Twelve micron thick mylar spacers were then positioned along the edge of one of the plates so no overlap onto the ITO occurred. The other plate was then carefully laid on top with the ITO stripes parallel though not completely overlapped to allow electrical contact to the ITO to be made.

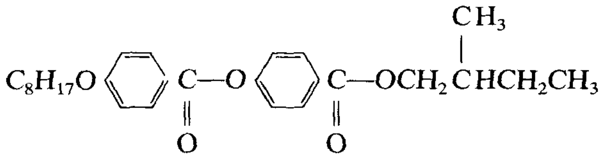
The two common edges were then glued together with epoxy adhesive. Finally, a T-type thermocouple was placed on the outside of the glass and glued in position with epoxy adhesive. The material was introduced into the cell by capillary action from the isotropic state.

The measurement of capacitance at a frequency of 1591.5 Hz (200 mV pk-to-pk) was performed on a Wayne Kerr autobalance universal bridge B642. The capacitance, coupled with a knowledge of the cell dimensions, leads to the dielectric constant. A 0–100 mV output from the bridge was amplified by a factor of 17 and the output from the amplifier fed to one of the A to D input ports of a BBC microcomputer where the data was recorded and stored for later processing.

For these measurements, the sample was contained in a laboratory oven in which the temperature could be slowly increased or lowered, in each case the rate of change of temperature was less than 1°C per minute.

RESULTS

The potential of the technique will be illustrated by showing the results from two compounds. The first is:

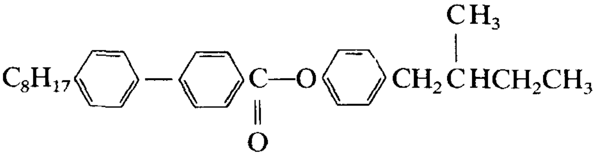


MOOBB

which has the following phase transitions

$$\begin{tikzcd}
\text{Crystalline} \arrow[rr, "33^\circ\text{C}"] & & \text{SmA} \arrow[rr, "58^\circ\text{C}"] & & \text{Isotropic} \arrow[dl, "58^\circ\text{C}"] \\
& \text{SmC} \arrow[ul, "18^\circ\text{C}"] \arrow[rr, "(32^\circ\text{C})"] & & \text{SmA} &
\end{tikzcd}$$

These phase transitions were taken from Reference 9. The other compound is



CE8

This has the following phases[11,12]

$$\text{Crystalline} \xleftrightarrow{48^\circ\text{C}} \text{SmG} \xleftrightarrow{62^\circ\text{C}} \text{SmJ} \xleftrightarrow{66^\circ\text{C}} \text{SmI}$$

$$\xleftrightarrow{71^\circ\text{C}} \text{SmC} \xleftrightarrow{81^\circ\text{C}} \text{SmA} \xleftrightarrow{138^\circ\text{C}} \text{Ch} \xleftrightarrow{141^\circ\text{C}} \text{Isotropic}$$

A plot of dielectric constant (ϵ_r) versus temperature for MOOBB and CE8 are shown in Figure 1 and Figure 2. The data for MOOBB (Figure 1) was obtained cooling the material from the isotropic liquid and two obvious discontinuities are apparent. These correspond to the isotropic–smectic A and smectic A–smectic C phase transitions.

Figure 2, showing data for CE8 obtained by heating the sample from room temperature should show seven discontinuities corresponding to the seven phase transitions. As can be seen at 50–55°C the crystal–smectic G transition is obvious and there are small changes between 130 and 140°C.

However, between 60 and 90°C where four phase transitions are expected the situation is rather obscure. If these dielectric constant data are now differentiated with respect to temperature and $d\epsilon_r/dT$ versus T plotted we obtain Figure 3 and Figure 4 for MOOBB and CE8 respectively. Figure 4 clearly shows seven peaks which correspond closely to the literature phase transition temperatures in CE8.

Figure 4 also illustrates the sensitivity and temperature resolution of the technique. The peak near 140°C is easily detectable and corresponds to a change in ϵ_r of 0.007 per °C, this equates to a capacitance change of 0.2 pF per °C. The peaks corresponding to the smectic J–

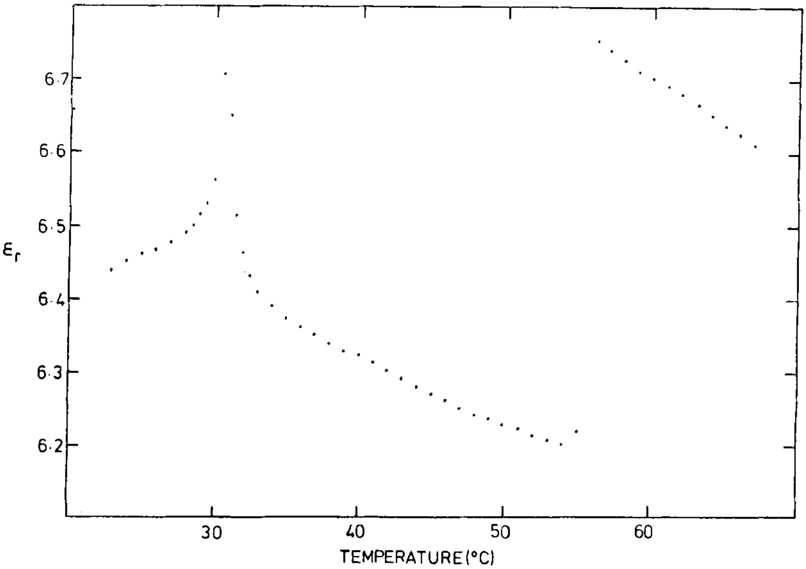


FIGURE 1 Temperature dependence of the dielectric constant of MOOBB at 1591.5 Hz.

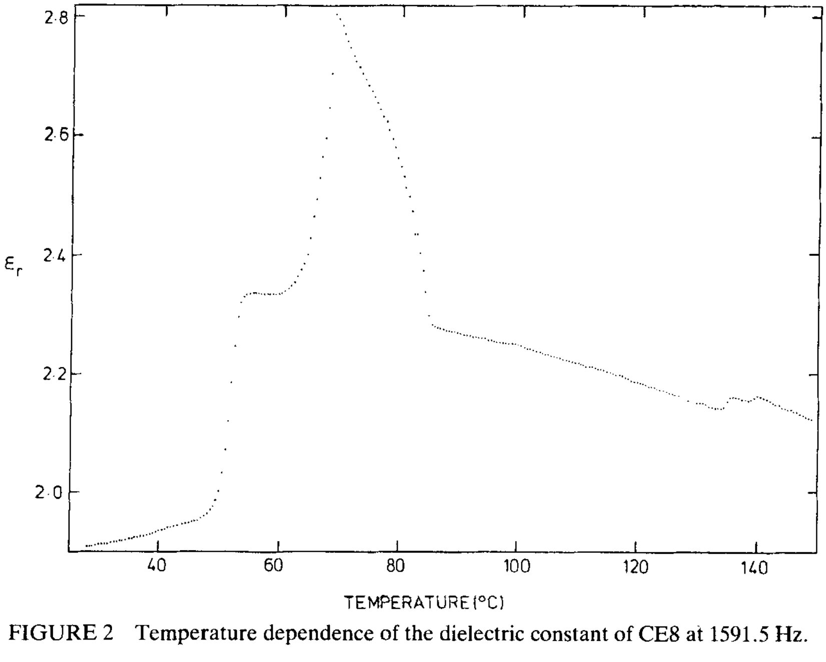


FIGURE 2 Temperature dependence of the dielectric constant of CE8 at 1591.5 Hz.

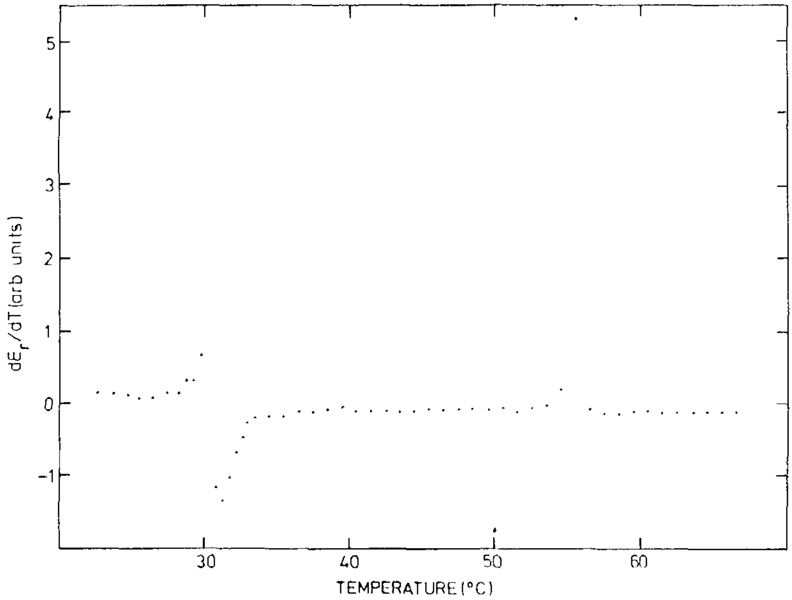


FIGURE 3 Differential dielectric constant versus temperature for MOOBB.

smectic I and smectic I–C transitions are clearly resolved and are separated by only 1.5°C.

Results for other compounds are shown in Table I. As can be seen the results from this work cover a wide variety of phase transitions and are in good agreement with literature values.

DISCUSSION

As shown in Figure 1 and Figure 2, there is a marked variation in dielectric constant with temperature. It has been reported that the magnitude of the dielectric constant is very much dependent on the orientation of the liquid crystal molecules, i.e. whether the long axis is parallel ($\epsilon_{\parallel}$) or perpendicular ($\epsilon_{\perp}$) to the applied electric field.[15] Any structural change which affects the molecular orientation will therefore necessarily alter the "average" dielectric constant (and hence the capacitance of the cell) which is detected by this technique. It was for this reason that no attempt was made to align the liquid crystal and run the risk of constraining it to a particular orientation. The effect will now be illustrated with reference to the phase transitions in MOOBB though similar arguments will apply to any phase transition in which a molecular re-orientation occurs. Recourse must

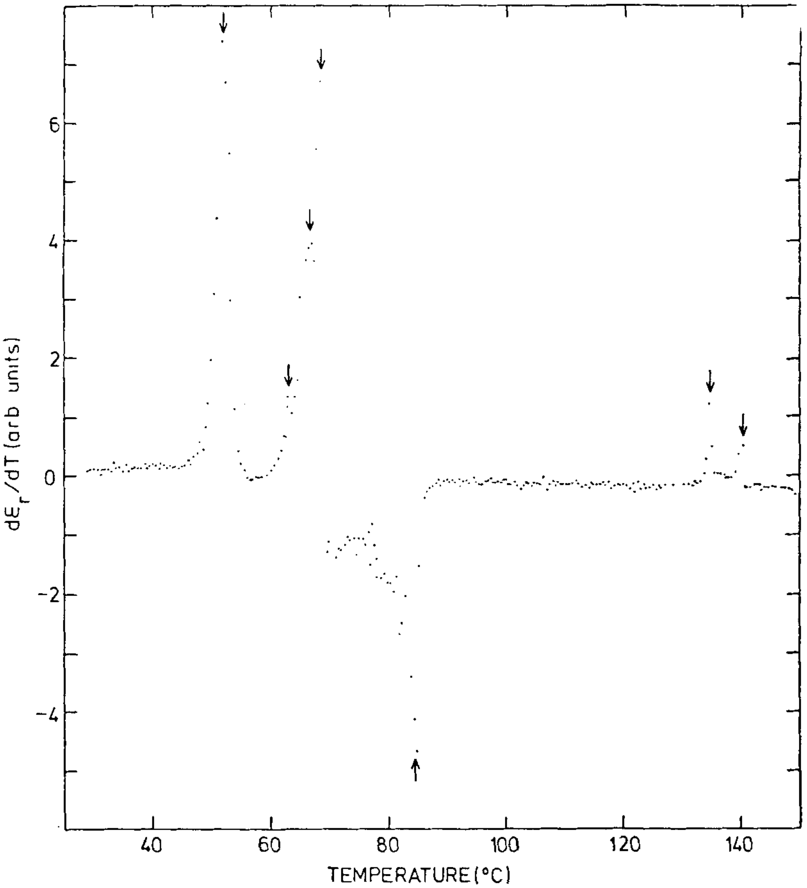


FIGURE 4 Differential dielectric constant versus temperature for CE8.

be made to the Clausius–Mosotti equation which relates the dielectric constant (ϵ) to the polarisability of the molecule (α)

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_i N_i\alpha_i$$

where N_i is the number of molecules per unit volume of polarisability α_i. Strictly, this equation applies to cubic or isotropic media but serves to qualitatively demonstrate the observed effects.

The total polarisability can be separated into three components

$$\alpha = \alpha_e + \alpha_l + \alpha_d$$

TABLE I

Results from this work compared to literature values

Chemical formula and acronym	Heat or cool	Phase transition	Phase transition temperature (°C)		Reference
			This work	Lit	
$\mathrm{C_8H_{17}PhPhCO_2PhCH_2CHMeEt}$	H	Cryst → SmG	51.75	48	11,12
		SmG → SmJ	62.75	62	
		SmJ → SmI	66.75	66	
		SmI → SmC	68.25	71	
		SmC → SmA	84.75	81	
		SmA → Chol	134.75	138	
(CE8)		Chol → Iso	139.75	141	
$\mathrm{C_5H_{11}OPhCHNPhC_7H_{15}}$	C	Iso → Nem	76.75	78	13
		Nem → SmA	62.75	65	
		SmA → SmC	53.25	54	
		SmC → SmB	49.75	51	
(50.7)		SmB → SmG	35.75	36	
$\mathrm{C_8H_{17}OPhCO_2PhCO_2CH_2CHMeEt}$	C	Iso → SmA	55.5	58	9
(MOOBB)		SmA → SmC	30.5	32	
$\mathrm{C_{12}H_{25}OPhCO_2PhCHCCNCO_2CH_2CHMeEt}$	C	Iso → SmA	90.5	89.4	10
		SmA → SmC	76.5	71.7	
(MCP 23)		SmC → Cryst	66.5		
$\mathrm{C_8H_{17}OPhCO_2PhOCH_2CHMeEt}$	C	Iso → SmA	58.25	58.5	14
		SmA → SmC	42.75	43.5	
(MOPAB 8)		SmC → Cryst	26.75		
$\mathrm{C_9H_{19}OPhCO_2PhOCH_2CHMeEt}$	C	Iso → SmA	59.25	60	14
		SmA → SmC	46.25	43.5	
(MOPAB 9)		SmC → Cryst	25.75		
$\mathrm{C_{10}H_{21}OPhCO_2PhOCH_2CHMeEt}$	C	Iso → SmA	62.75	65	14
		SmA → SmC	49.75	50.2	
(MOPAB 10)		SmC → Cryst	30.25		

where α_e is the electronic, α_I the ionic and α_d the dipolar (sometimes known as orientational) polarisability. The contribution from each component depends on the working frequency. At the frequency used in this work (1591.5 Hz) $\alpha_e > \alpha_d > \alpha_I^2$.

For non-ionic mesogens the contribution from α_I will be zero. In general, thermotropic liquid crystals have a long aromatic (delocalised) core in which the π electron cloud is easily distorted by an electric field. The electronic polarisation is greater along the length of the core than across its width i.e. $\alpha_{e_\parallel} > \alpha_{e_\perp}$. Therefore there is a tendency for these molecules to align with their long axes parallel to the applied electric field. In MOOBB (and indeed most smectogens) the largest dipole moment arises from an outboard dipole (in this case, the carbonyl group of the ester linkage) and is normal to the long molecular axis. Because of these strong transverse dipoles $\alpha_{d_\perp} > \alpha_{d_\parallel}$.

In the isotropic phase the molecules are randomly orientated and the total polarisability arises from contributions from both α_e and α_d. On cooling the isotropic liquid the smectic A phase separates out in the form of batonnets (see Reference 16 for a description of batonnets) which coalesce and build up the focal conic fan texture. Within each batonnet (or fan) the molecules are on average parallel to the cell wall so the contribution to the polarisability comes mainly from α_d and results in a reduction of the dielectric constant. The increase in the dielectric constant as the temperature decreases in both the isotropic and smectic A phases is probably due to two co-operating effects. Firstly by an increase in polarisation due to thermal agitation as predicted by the Langevin–Debye relation

$$\alpha = \frac{\mu^2}{3kT}$$

where μ = Dipole moment

k = Boltzman constant

T = Absolute temperature

Also thermal contraction of the cell spacing would lead to a similar trend in dielectric constant versus temperature.

The variation of the dielectric constant around the smectic A to smectic C transition is not so easily explained in molecular terms. A complicating factor is that our sample of MOOBB is a pure optical isomer so we are dealing with a non-ferroelectric to ferroelectric phase transition as well as the structural change. However, the behaviour of the dielectric constant at the isotropic–smectic A and smectic A–smectic C phase transitions can be understood qualitatively by considering the thermodynamics of phase transitions. Isotropic to smectic A is a first order transition while smectic A to smectic C is generally considered to be second order, though from an early stage in the development of the theoretical description of phase transitions doubt was cast on the existence of a genuine second order transition.[4,17] For a first order transition a plot of the Gibbs free energy (G) against temperature shows a discontinuity in the gradient at the transition point. This leads to a sudden change in thermodynamic properties such as entropy $(\delta G/\delta T)_P$ and volume $(\delta G/\delta P)_T$. Since the dielectric constant is related to the Gibbs free energy[18] then a sudden change in the dielectric constant at the isotropic–smectic A transition is expected.

In a truly second order transition there is no predicted discontinuity in the Gibbs free energy versus temperature curve. Since it is unlikely that the smectic A–smectic C transition is exclusively second order[4,17] some change in the thermodynamic properties and hence the dielectric constant should be expected. This is observed for the transition in CE8 (Figure 4) which is a racemate, so a ferroelectric–non-ferroelectric phase transition does not occur. In MOOBB there is a different shape in the dielectric constant versus temperature curve at the smectic A–smectic C transition. The shape is similar to that found for the inorganic crystal $BaTiO_3$, at its non-ferroelectric–ferroelectric phase transition (which is known to be first order).[19,20] The change is much smaller for the liquid crystal probably due to a higher degree of disorder than in the inorganic crystal and the fact that the transition (in liquid crystals) does not have a well defined order. Indeed, the shape of the dielectric constant versus temperature curve suggest the smectic A to ferroelectric smectic C phase change is partially first order in nature.

CONCLUSIONS

It has been demonstrated that a wide range of phase transitions can be detected using temperature-dependent dielectric constant (TDDC) data and any phase transition involving a structural re-arrangement can in principle be detected. It has also been shown that this technique gives a very clear indication of the smectic A–smectic C transition, which can prove difficult to detect with DSC. Figure 3 and Figure 4 show that the phase transitions isotropic–cholesteric and cholesteric–smectic A give quite small peaks (as does the isotropic–nematic and nematic–smectic A in 50.7) and are hence more difficult to detect than the larger smectic I–smectic C and smectic C–smectic A (for example). This does not mean that these transitions will be difficult to detect *at all frequencies* since the dielectric constant is frequency dependent, its change on going through phase transitions will also be frequency dependent. No work has been done on the frequency dependence of the magnitude of the transitions and it may prove to be a valuable extension of this technique. It is variables such as this that give this technique a flexibility that DSC and optical determinations do not possess.

Acknowledgments

The author acknowledges the part financial support of the Department of Trade and Industry under the JOERS scheme.

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