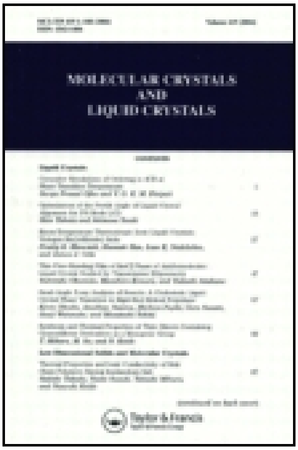

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Dielectric Studies on Two Isomeric Cyano Ester Homologous Series

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We have studied the static dielectric permittivities of two homologous series of compounds, viz., 4-cyanophenyl 4'-*n*-alkoxybenzoates (CPnOB) and 4-*n*-alkoxyphenyl 4'-cyanobenzoates (nOPCB). These are biaromatic compounds with a terminal cyano group, but the ester linkages in the two series are oppositely disposed. For both series of compounds, the mean permittivity shows a jump at the nematic–isotropic transition that increases with increasing chain length. The pretransitional effects in the isotropic phases of the compounds CPnOB, wherein the longitudinal component of the dipole moment of the ester linkage is additive with regard to the cyano end-group, are found to be nearly one order of magnitude larger than those seen in the case of the nOPCB compounds.

INTRODUCTION

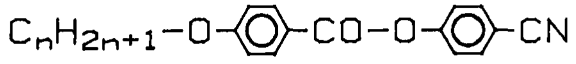
The occurrence of the reentrant nematic phenomenon[1] in strongly polar liquid crystals can be attributed to the existence of antiparallel pairing[2,3] of near-neighbor molecules. In an attempt to prepare materials in which the dipolar forces within the constituent molecules can be altered and hence the degree of pairing in the nematic phase can be changed, Göbl-Wunsch et al.[4] and Goodby et al.[5] synthesized two homologous series of cyano esters, viz., 4-cyanophenyl 4'-*n*-alkyloxybenzoates (CPnOB) and 4-*n*-alkyloxyphenyl 4'-*n*-cyanobenzoates (nOPCB). Both of these are biaromatic compounds; the dipole moment of the ester linkage group in the former case is disposed additively with respect to the cyano end group, while in the latter series it opposes the direction of the dipole of the cyano group. X-ray studies on these materials[6,7] have shown that the d/l values in the two series, nOPCB and CPnOB, are about 1.4 and 1.23, respectively. Here, d is the layer spacing measured in the smectic A phase and l is the length of a molecule in its most extented conformation measured using a Dreiding model. These results clearly show that the "degree of molecular overlap" is substantially different for the two series, this being attributable to the differences in the dipolar correlations of the longitudinal dipole moments of adjacent molecules. It was also shown[6,7] that the layer spacing is independent of temperature for all compounds of the CPnOB series, while it was found to be slightly dependent on temperature for the nOPCB series. Since it is known from earlier studies[8–10] that the dielectric behavior of strongly polar molecules can be correlated to structural changes in these systems, it is of interest to see if the differences in molecular packing between members of the CPnOB and nOPCB series lead to a difference in their dielectric properties. In view of these factors, we have undertaken a detailed study of the dielectric permittivities of the different members belonging to the above mentioned homologous series. The results of these investigations are presented in this paper.

EXPERIMENTAL

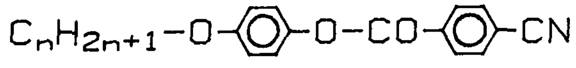
We have studied four compounds belonging to each of the homologous series, *n* = 8 to 11 of the CPnOB series and *n* = 6 to 9 of the nOPCB series. The transition temperatures for these substances are listed in Table I. The *n* = 8 member of the CPnOB series exhibits only a nematic phase, while the other homologues show in addition a smectic A phase. In the case of the nOPCB series, the 6th member has only a nematic phase, the 9th member only a smectic A phase, and the *n* = 7 and *n* = 8 materials exhibit both smectic A and nematic phases. It must also be mentioned that although microscopic observation showed a smectic C phase for n = 7 to n = 12, owing to the extremely highly metastable nature of this phase, we could not make any dielectric measurement for the C phase.

TABLE I

Phase transition temperatures of CPnOB series and nOPCB series; values given in °C; values in ( ) denote monotropic transitions



n	K		S_A		N		I
CP8OB	·	74	—		·	84.0	·
CP9OB	·	78	·	(59.3)	·	83.0	·
CP10OB	·	78	·	79.2	·	86.0	·
CP11OB	·	81	·	85.8	·	86.2	·
CP12OB	·	72	·		—	87.2	·



n	K		S_A		N		I
6OPCB	·	85	—		·	95.2	·
7OPCB	·	71	·	80.1	·	94.6	·
8OPCB	·	62	·	90.2	·	95.5	·
9OPCB	·	69	·		—	95.6	·

The experimental set up used in our dielectric studies has already been described elsewhere[11] and will not be repeated here. The only additional feature is that in the case of 9OPCB, which has no nematic phase, a combination of surface treatment and a magnetic field was adopted to ensure a good alignment in the smectic A phase.

RESULTS AND DISCUSSION

A. CPnOB series, *n* = 8 to 12

The variation of the static permittivities ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) and the mean permittivity $\bar{\varepsilon}$ [$= (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$] in the nematic and smectic A phases of the four compounds studied is shown in Figure 1 along with the data for the isotropic phase (ε_{is}). The following features are clear from these figures:

1) All the materials exhibit a large anisotropy, as indeed is expected, because the longitudinal component of the dipole moment of the bridging group is additive with respect to the cyano group.

2) The temperature dependence of $\varepsilon_{\perp}$ is essentially similar for all the substances, regardless of whether a smectic A phase exists or not.

3) On the other hand, the temperature variation of $\varepsilon_{\parallel}$ seems to be influenced by the occurrence of the smectic A phase. For CP8OB which has only a nematic phase, as well as for CP9OB exhibiting both N and A phases, $\varepsilon_{\parallel}$ shows a continuous increase with decreasing temperature. The lack of influence of the A phase on the behavior of $\varepsilon_{\parallel}$ in these compounds can be attributed to the large range (24 K) of the N phase; this is also confirmed by the fact that for both CP10OB and CP11OB, for which the range of the N phase is much smaller (7 K and 0.4 K, respectively), the behavior of $\varepsilon_{\parallel}$ is strongly influenced by the appearance of the smectic A phase. There is a decrease of $\varepsilon_{\parallel}$ at the N–A transition, evidently due to the increased antiparallel correlation in the A phase. The decrease of $\varepsilon_{\parallel}$ is more pronounced in the case of CP11OB which has an extremely narrow range of the N phase and can perhaps be attributed to the reported first order nature of the A–N transition.[11]

4) The dielectric anisotropy $\Delta\varepsilon$ decreases continuously with increasing chain length. This behavior has been observed in the case of other strongly polar systems.[12]

We shall now examine the data near the nematic–isotropic (N–I) transition more closely in order to compare the extent of antiparallel correlations, i.e., the strength of the pretransitional effects for the successive homologues. For this purpose we have plotted in Figure 2(a) the value of the mean dielectric constant $\bar{\varepsilon}$ along with the data for ε_{is} for a temperature range of 5 K on either side of T_{NI}. It is seen that, for all the systems, there is a discontinuity in $\bar{\varepsilon}$ at the clearing point. It may be pointed out that this discontinuous jump of $\bar{\varepsilon}$ was predicted theoretically[2] and was attributed to the existence of antiparallel short range correlations which decrease as T_{NI} is approached. Such a jump has been observed for a number of cyano compounds.[13] The important feature of our results in Figure 2(a) is that the

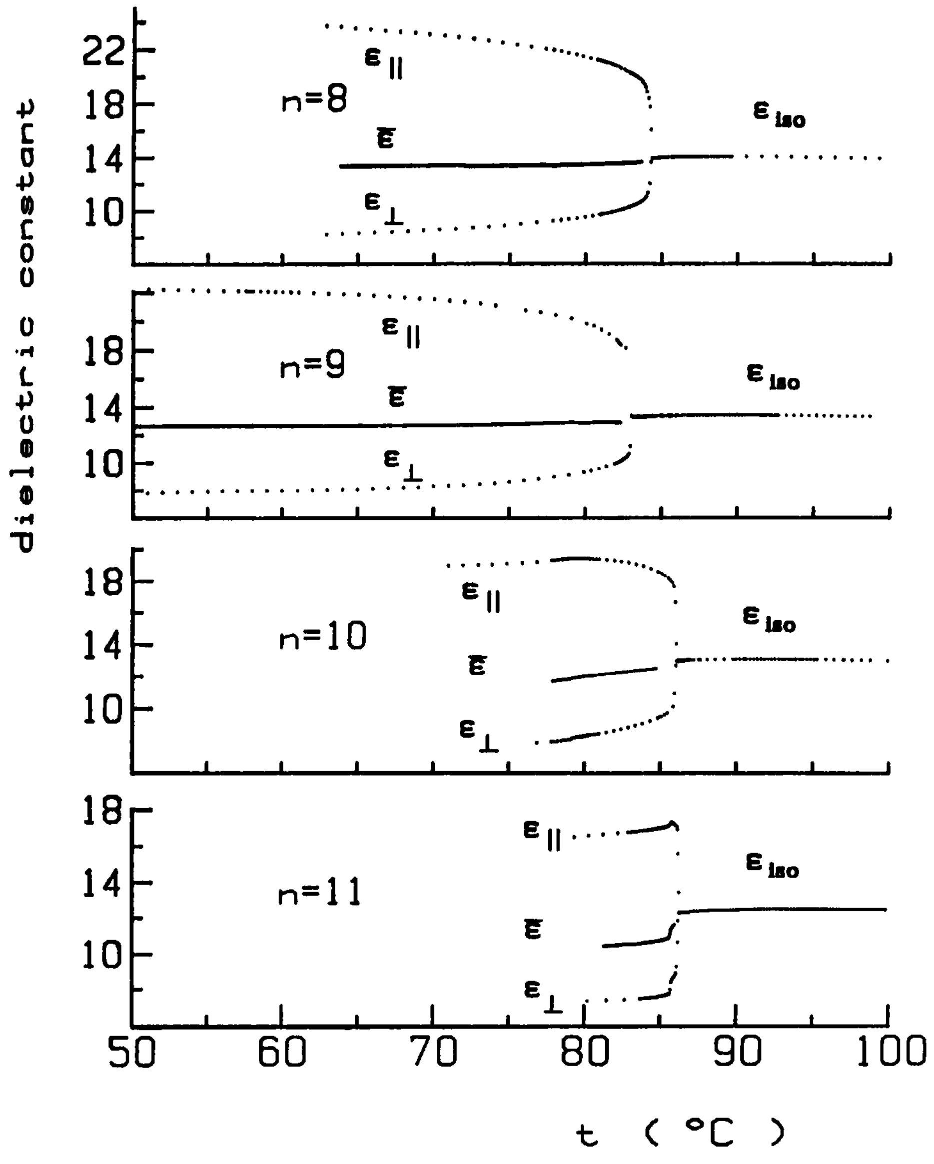


FIGURE 1 Temperature dependence of the quasistatic dielectric permittivity of CPnOB series, n = 8 to 11.

magnitude of the jump in $\bar{\varepsilon}$ at T_{NI} increases with increasing chain length. In the case of CP11OB, for which data have been shown for the A, N and I phases, such a jump is seen at the A–N transition also. These results show that the strength of the antiparallel correlations in the nematic phase increases with increase in the chain length n. Since increasing n is also concomitant with decreasing nematic range or increasing smectic order, we can, therefore, infer that the increase in the mag-

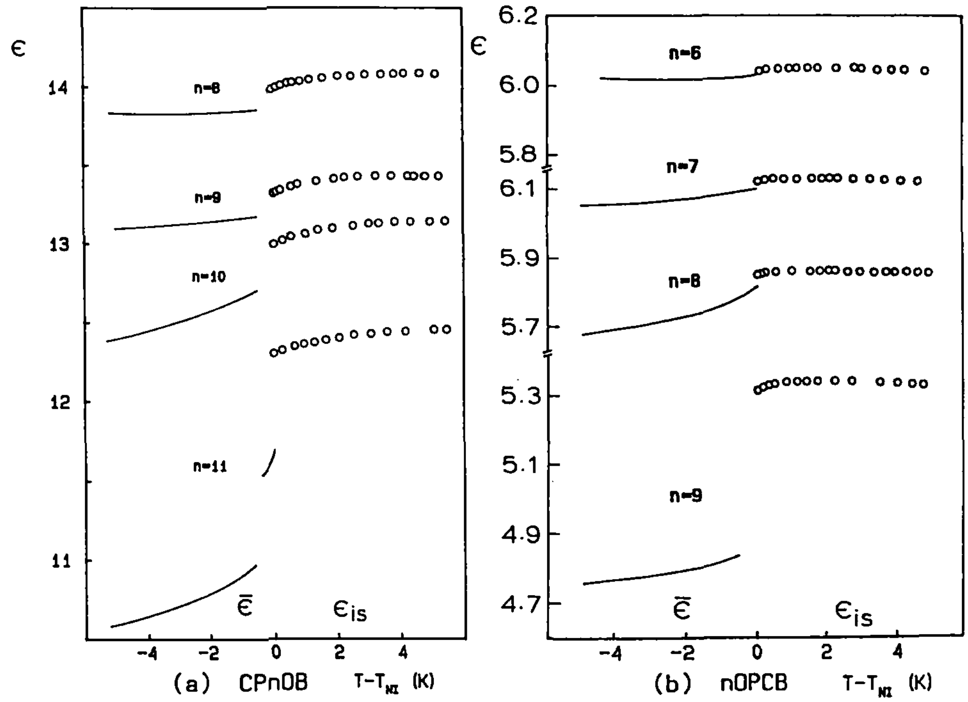


FIGURE 2 Dielectric permittivity of (*a*) CPnOB series and (*b*) nOPCB series around the clearing point.

nitude of the jump in $\bar{\varepsilon}$ at T_{NI} is due to the enhanced smectic-like ordering in the nematic phase.

Finally, we shall discuss the behavior of ε_{is} for the CPnOB compounds. For the sake of convenience of discussion, these data have been shown on an enlarged scale in Figure 3(a); for the sake of comparison this figure also gives the data for CP12OB, which exhibits the A–I transition. (It should be pointed out that it was not possible to obtain a well aligned A phase and hence the data for the A phase of this compound are not given in Figure 2.) Pretransitional effects are clearly seen for all the substances. It may be recalled that the existence of such an effect within the isotropic phase of materials was first reported by Bradshaw and Raynes[13] and later confirmed by Thoen and Menu.[14] In order to compare the extent of these pretransitional effects on ε_{is} for the different substances, we have evaluated the quantity $\Delta\varepsilon_{is} = ((\varepsilon_{is})_{max} - \varepsilon_{is})/(\varepsilon_{is})$, where ε_{is} is the value at T_{NI} and $(\varepsilon_{is})_{max}$ is the maximum value of the permittivity in the isotropic phase. The values of $\Delta\varepsilon_{is}$ for the CPnOB series of compounds (given in Table II) are similar to those seen for the alkylcyanobiphenyl.[10] Another feature of these results is that this ratio, which can be taken as a measure of the strength of the pretransitional effect in the isotropic phase, increases with increasing chain length n up to $n = 11$, after which it appears to decrease slightly for $n = 12$, a pure smectic material. This decrease, which is quite small, is perhaps due to the increased strength of the isotropic–mesophase

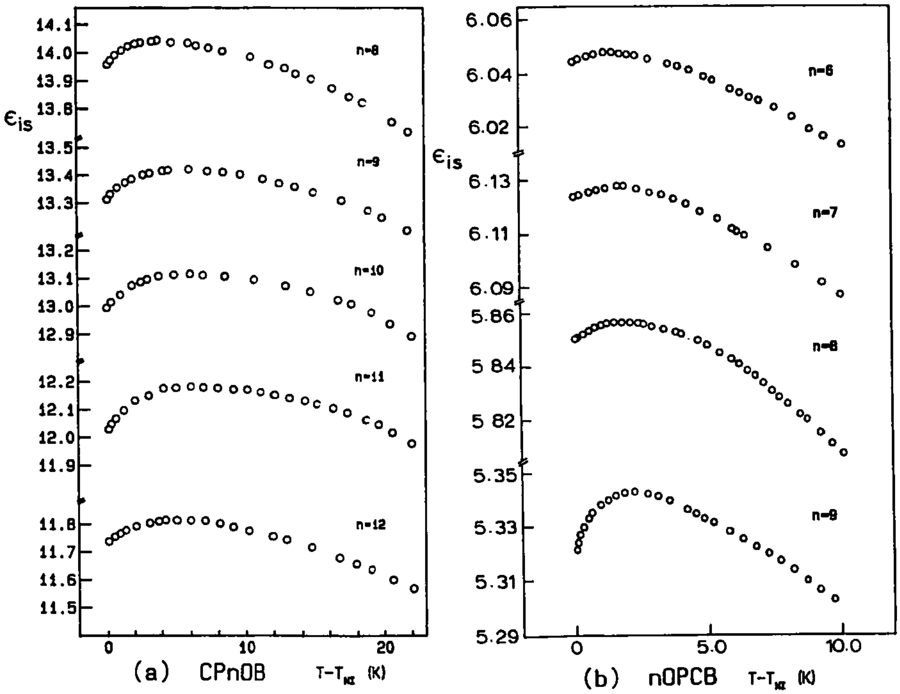


FIGURE 3 Dielectric permittivity of (*a*) CPnOB series and (*b*) nOPCB series in the isotropic phase.

transition. It is relevant to remark that the earlier experiments of Bradshaw and Raynes[13] on the nCB series also appear to show the same behavior.

B. nOPCB series, n = 6 to 9

We shall now discuss the results for the nOPCB series of compounds (n = 6 to 9). Figure 4 shows the temperature variation of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\bar{\varepsilon}$ and ε_{is}.

The data for $\bar{\varepsilon}$ and ε_{is} close to T_{NI} are presented in Figure 2(b), while the data only for ε_{is} are shown on an enlarged scale in Figure 3(b). On the whole, the results on compounds of the nOPCB series are similar to those of the CPnOB series discussed in the preceding section. We shall therefore comment only on a few

TABLE II

Magnitude of the pretransitional effect in the dielectric permittivity

CPnOB		nOPCB	
n	$\Delta\varepsilon_{is}$ (%)	n	$\Delta\varepsilon_{is}$ (%)
CP8OB	0.73	6OPCB	0.056
CP9OB	C.90	7OPCB	0.07
CP10OB	1.07	8OPCB	0.13
CP11OB	1.37	9OPCB	0.48
CP12OB	0.74		

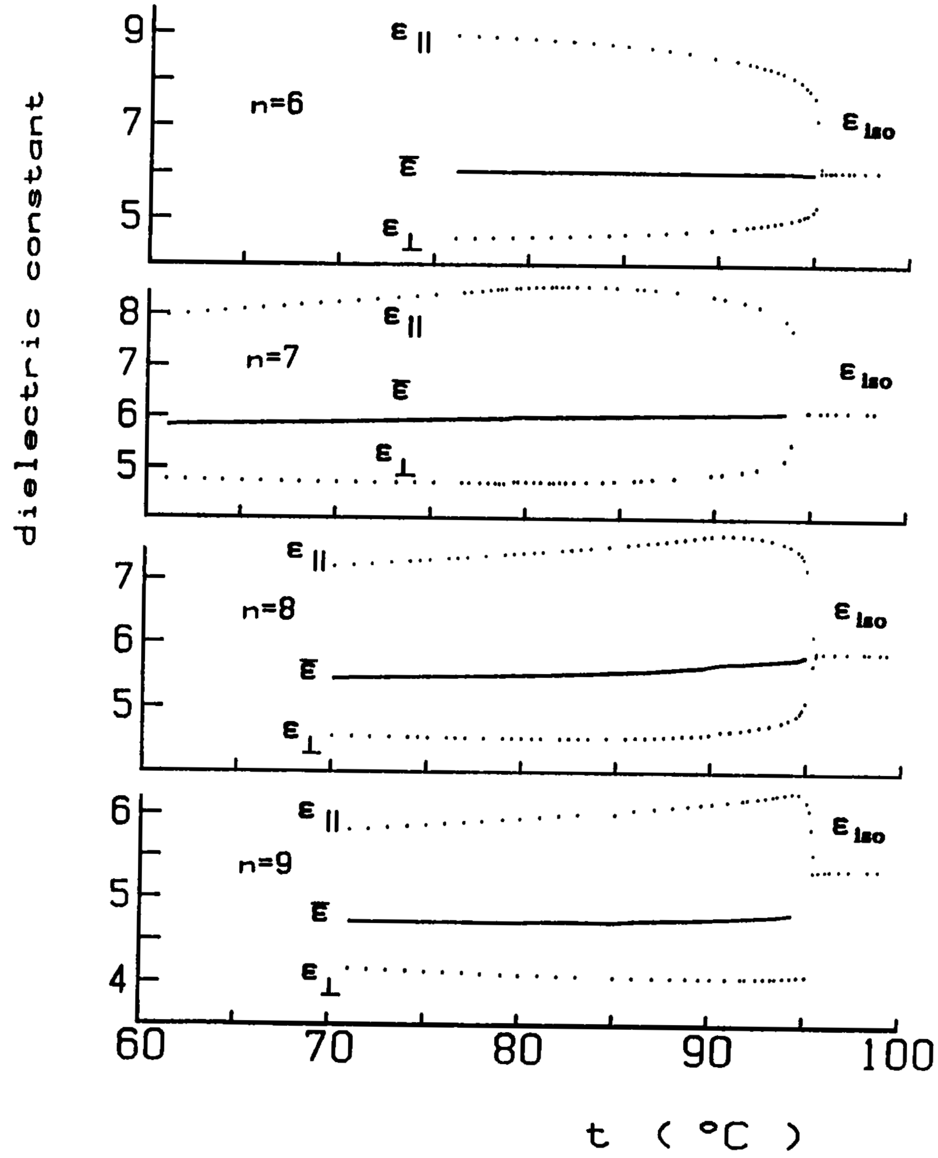


FIGURE 4 Temperature dependence of the quasistatic dielectric permittivity of nOPCB series, n = 6 to 9.

features of the results which permit us to compare the behavior of the two homologous series:

1) The behavior of $\varepsilon_{\parallel}$ is the same for both the series. There is a decrease in the value of $\varepsilon_{\parallel}$ at T_{NA} and the decrease becomes slowed within the smectic A phase.

2) There is a marked difference in the behavior of $\varepsilon_{\perp}$. In the case of the nOPCB series, $\varepsilon_{\perp}$ shows an increase with decrease of temperature in the A phase, while

in the case of the CPnOB series there is only a saturation or a decrease in the $\varepsilon_\perp$ value. The increase in $\varepsilon_\perp$ in the former case may be due to an increase in the correlation of the transverse component of the bridging group dipoles caused by the expansion of the layer spacing. The layer spacing being constant with temperature for CPnOB,[6,7] there is no pronounced change in correlation of the ester linking groups.

3) The dielectric anisotropy $\Delta\varepsilon$ of the nOPCB series is much smaller than that of the CPnOB series. It decreases with increasing *n* in both cases. There is, however, a subtle difference in the behavior of $\Delta\varepsilon$ between the two series. In the case of CPnOB, $\Delta\varepsilon$ shows a clear increase with decrease of temperature below T_{NA} and tends to saturate at lower temperatures. Compounds of the nOPCB series show a pronounced decrease in $\Delta\varepsilon$ throughout the A phase. A notable feature of our results is that the temperature at which $\Delta\varepsilon$ attains saturation seems to move closer to T_{NA} as the chain length increases.

4) The discontinuous jump in $\bar{\varepsilon}$ at the transition to the isotropic phase increases with increasing *n* for both series.

5) Although compounds of both series show pretransitional effects in the isotropic phase, the effect in an nOPCB is much less pronounced compared to a CPnOB. As shown in Table II, the value of $\Delta\varepsilon_{is}$ for the former is nearly one order of magnitude smaller, the difference becoming more pronounced with increasing *n*.

In conclusion, our studies of the two homologous series of isomeric cyano esters show that the dielectric behavior of these systems is qualitatively similar, albeit there are subtle differences in the behavior of $\varepsilon_\perp$ and $\Delta\varepsilon$ in the A phases. Although the disposition of the bridging dipoles affects the magnitude of the dielectric constant, it does not seem drastically to affect the overall dielectric behavior. Similar studies of other homologous series of compounds with somewhat different molecular structures are in progress.

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