Electrical Dark- and Photo-conductivities of 2-(*p*-Decyloxybenzilideneamino)-9-fluorenone in the Nematic State

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(Received October 1, 1982)

The electrical conductivity of 2-(*p*-decyloxybenzylideneamino)-9-fluorenone (DBAF), which has a large π-electronic group, was investigated in the nematic state. The dark conductivity showed a positive anisotropy and was attributed to ionic conduction. The photocurrent was observed in the absorption region of DBAF and was enhanced by doping with 2,4,7-trinitro-9-fluorenone. The photocarriers seem to be generated from the excited state of DBAF by one photonic process.

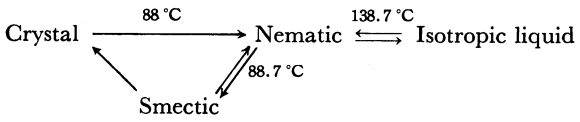
Electrical dark-conductivity in liquid crystals has been studied extensively[1-5] and attributed to ionic conduction on the basis of both the conductivity anisotropy[2,3] and the temperature dependence of the carrier mobility.[4,5] On the contrary, photoconductivity in liquid crystals has never been reported until now except for the photocurrent due to the photoinjection of charge carriers from an electrode.[6,7] This is probably because the liquid crystals investigated to data have had only small π-electronic groups, such as a benzene ring. In this paper, we investigated the dark- and photo-conductivities of 2-(*p*-decyloxybenzylideneamino)-9-fluorenone (DBAF), which has a large π-electronic group, in the nematic, monotropic smectic, and isotropic liquid states.

Experimental

The DBAF was prepared according to the literature[8] and was recrystallized several times from an absolute ethanol solution. The purity of the DBAF was satisfactory, judging from the analysis by means of differential scanning calorimetry and high-performance liquid chromatography. The *p*-methoxybenzylidene-*p*-butylaniline (MBBA) was obtained commercially and was purified by means of high-vacuum distillation. The sample was sandwiched between two nesa-coated glass electrodes with a Myler spacer 20—100 μm thick. The effective area of the cells was typically 1 cm^2. The capacitance and DC conductivity measurements were carried out under an argon atmosphere.

Results and Discussion

The phase transitions were as follows:



Alignment of the Molecules in Nematic State. The magnetic field aligns the long axes of the liquid crystal molecules along its direction.[9] Figure 1 shows the variation in the specific dielectric constant ε with the magnetic field H. A homogeneous or homeotropic alignment of the molecules in the nematic state was achieved by the magnetic field of 0.4 T perpendicular to or parallel to the applied electric field E. The negative dielectric anisotropy of DBAF ($\Delta\varepsilon = -1.65$ at 100 °C) is larger than that of such typical Schiff-base-type liquid crystals as MBBA,[2,9] because of the presence of a carbonyl group nearly perpendicular to the long molecular axis.

Dark Conductivity. The dark conductivity σ was measured for the homogeneous or homeotropic alignment, and labelled $\sigma_\perp$ or $\sigma_{//}$ respectively. The dark current obeyed Ohm's law in the fields less than 10^4 V/cm in every state. Figure 2 shows the temperature dependence of the dark conductivity and its anisotropy ratio, $R = \sigma_{//}/\sigma_\perp$. At the crystal-nematic phase transition, σ increased abruptly and showed a sharp peak which disappeared with an increasing voltage. This peak current seems to be caused by the abrupt change in the direction of the dipole-moment due to the change in molecular direction at the phase transition.[5] At the nematic-isotropic transition, $\sigma_{//}$ decreased appreciably, while $\sigma_\perp$ hardly changed. In the nematic state, σ was in the order of 10^{-10} Ω^{-1} cm^{-1} and ΔE_a was 0.5 eV. These values of σ and ΔE_a are comparable to those reported for typical nematic liquid crystals.[1-4] The temperature dependence of R is also similar to that reported for the Schiff-base-type liquid crystals;[2,3] that is, R is larger than unity in the nematic state, although it, because of a pretransitional effect, decreases below unity when approaching the transition to a smectic state. These results indicate that the dark conductivity of DBAF in nematic and isotropic states is caused by the ionic mechanism previously reported for conventional liquid crystals,[2-5,10] in spite of the presence of a large π-electronic group.

Photoconductivity in Nematic State. The stady-state photocurrent was reached in a few minutes when a cell was irradiated. Although the photocurrent in the crystal state obeyed Ohm's law, that in the nematic state showed a very complicated dependence on the field, as shown in Fig. 3. After reaching a maximum, the photocurrent decreased and then levelled off with an increasing field. At present, we have no explanation for this behavior; therefore, we restricted the experiments to the low-field range where the photocurrent increased roughly linearly with an increasing field. The photocurrent was roughly proportional to the light intensity and was observed in the spectral region of DBAF, as shown in Fig. 4, indicating that the photocurrent is caused by the light absorption of DBAF itself. The photocurrent increased step-by-step by a factor of 100 at the crystal-nematic phase transition, and it was almost independent of the temperature in the nematic state.

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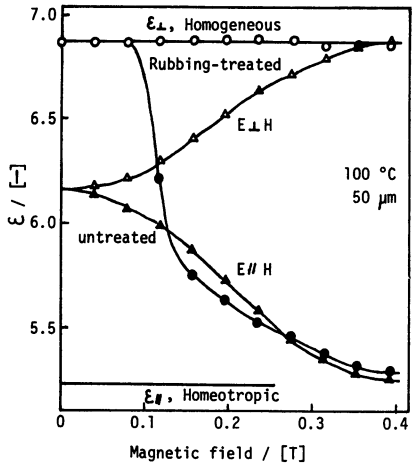

Fig. 1. Magnetic field dependence of specific dielectric constant ε at the frequency of 1 kHz.
○, ●: A rubbing-treated cell, △, ▲: an untreated cell (open symbols, $E \perp H$; closed symbols, $E//H$).

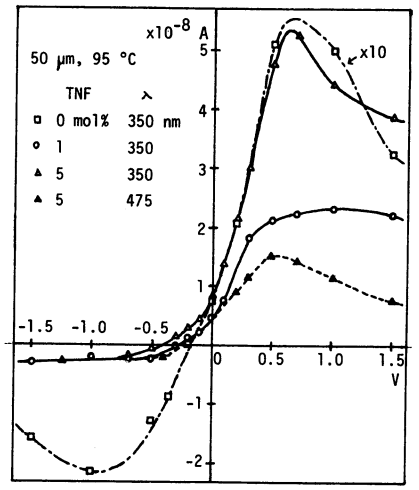

Fig. 3. Electric field dependence of the photocurrent for the celles undoped and doped with TNF.

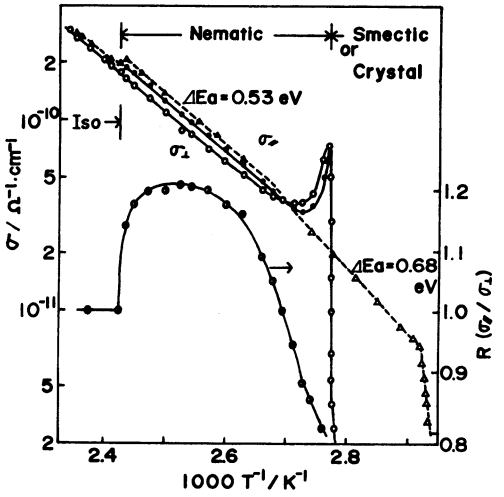

Fig. 2. Temperature dependence of dark conductivity σ and its anisotropy ratio R.
—○—, --△--: $\sigma_\perp$, —●—, --▲--: $\sigma_{//}$ (circle symbols, on a heating run; triangle symbols, on a cooling run). —◑—: R on a heating run. In liquid state, $\sigma_{//}$ was identical with $\sigma_\perp$. In nematic state, the line --△-- was almost overlapped with the line —●—.

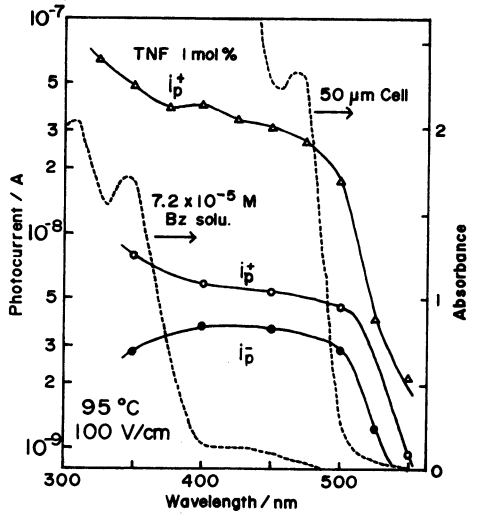

Fig. 4. Spectral dependence of the photocurrent and the absorption spectra.
Light intensity was 1×10^{15} photons/cm² s. The dotted lines were the absorption spectra of the benzene solution and of a cell of 50 μm thickness. —○—, —●—: An undoped cell, —△—: a cell doped with 1 mol% of TNF.

Although nematic MBBA did not show the photocurrent, the nematic mixtures of MBBA containing more than 10 mol% of DBAF showed the photocurrent in the absorption region of DBAF. The photocurrent increased appreciably with an increase in the DBAF content, but it was too small to be measured in detail. More detailed measurements were done for the pulse photoconduction induced by a N_2 gas laser and will be reported elsewhere.[11]

DBAF formed a charge-transfer complex with a strong electron acceptor. 2,4,7-Trinitro-9-fluorenone (TNF) was chosen as an acceptor, because it was fairly soluble in the nematic phase of DBAF. The complex of DBAF with TNF showed a charge-transfer absorption band at 485 nm in a dichloroethane solution. Doping with TNF by 1—5 mol% enhanced the photocurrent for the positive-electrode illumination (abbreviated as i_p^+) by a factor of 4—10, as shown in Figs. 3 and 4, while it hardly changed either the dark current or the photocurrent for the negative-electrode illumination (i_p^-).

The following photocarrier-generation process for nematic DBAF and its mixture with MBBA is suggested from the results presented above, with reference to the processes previously proposed for aromatic molecules in solutions[12,13] and in amorphous films.[14] In the first step, DBAF molecules absorb light, creating a molecular excited state. An excited DBAF molecule can react with either the electrode or an electron acceptor molecule, such as TNF and O_2, to give the original photocarriers. The original photocarrier species may thus be supposed to be the cation radical of DBAF and the anion radical of either DBAF or an electron

acceptor. The nature of the carrier-transport process (ionic diffusion or electronic hopping) in the photoconduction is still in question and so is under investigation.[11]

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