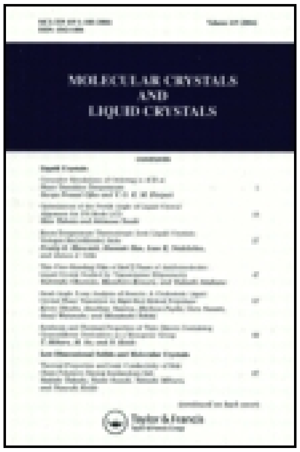

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphic and Photoconducting Behavior of 2-(2-Hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles

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To cite this article: Yo Shimizu , Kunio Shigeta & Shigekazu Kusabayashi (1986): Mesomorphic and Photoconducting Behavior of 2-(2-Hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles, Molecular Crystals and Liquid Crystals, 140:2-4, 105-117

To link to this article: http://dx.doi.org/10.1080/00268948608080146

Mol. Cryst. Liq. Cryst., 1986, Vol. 140, pp. 105–117
0026-8941/86/1404–0105/$20.00/0

Printed in the United States of America

Mesomorphic and Photoconducting Behavior of 2-(2-Hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles

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(Received March 10, 1986; in final form May 26, 1986)

The mesomorphic properties of 2-(2-hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles were investigated and the photoconducting behavior of the crystalline, nematic and isotropic liquid phases were compared for the pentyloxy compound. It was found that the behavior in the nematic phase is comparable with that in the isotropic liquid phase, both being fluid, rather than that in the crystalline phase. The carrier transport mechanisms and the carrier species are implied to be ionic. The current-voltage characteristics showed a new behavior in the fluid states, being similar to that of the negative resistance.

Keywords: mesomorphic properties, photoconducting behavior, 9-methylcarbazole, negative resistance, nematic phase, smectic A phase

INTRODUCTION

Nematic liquid crystals with rod-like molecular shapes have been used as switching devices by means of an applied electric field. Therefore, the darkcurrent behavior of the nematic state has been mainly studied so far, while the photocurrent one has been reported in only a few papers.[1,2,3]

Studies of the photoconducting behavior in mesophases are interested in (1) searching for some new functions of mesophases, (2) researching the fundamental differences among mesophases, crystalline and isotropic liquid phases in the sense of electric conduction.

Of the photoconduction in mesomorphic states, Kusabayashi and Labes reported first for nematic, smectic and cholesteric materials that a photo-response was found in several rod-like liquid crystals.[1]

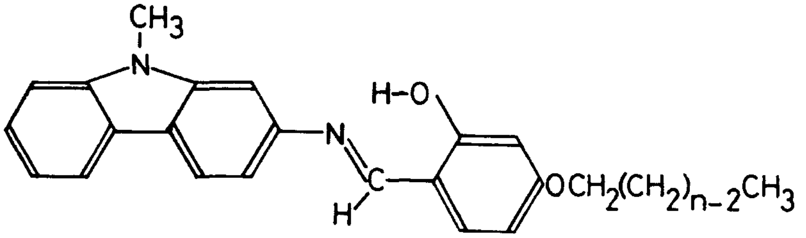
Recently, in regard to the photocarrier transport mechanism for the photoconductive 2-(4-decyloxybenzylideneamino)fluorenone in the nematic and smectic states, it has been suggested that the nature of the photocarrier is not electronic but ionic, and that the carrier species are $O_2^{\overline{\cdot}}$ and a cation radical which are derived from oxygen molecules contained in the system and from the compound itself, respectively,[2] and it also has been suggested that the photocarrier is generated from the excited state by one photonic process.[3]

On the other hand, Poly(*N*-vinylcarbazole) has been extensively studied as an available photoconductive polymer and the carrier generation and transport mechanisms were revealed.[4,5]

The liquid crystalline system containing carbazole as a dopant was also investigated, and the photo-response and photoconductivity-voltage characteristics were reported.[6]

Any results, however, have not been sufficiently obtained from a viewpoint of differences of photocurrent behavior among mesophases, crystals and the isotropic liquid phase.

In order to compare the behavior of photoconduction in mesophases with that of crystalline and isotropic phases, a homologous series of 2-(2-hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles was prepared and investigated on the mesomorphic properties. The pentyloxy compound was served for measurements of photoconducting behavior.



2-(2-hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles
n = 4,5,6,7,8,9,10,11,12 and 14.

EXPERIMENTAL

Materials

2-(2-Hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles:

The Schiff's base compounds were prepared by refluxing the absolute ethanol solution of the equimolar 2-amino-9-methylcarbazole and the corresponding 4-alkoxybenzaldehyde and recrystallized from absolute ethanol more than three times. 2-Amino-9-methylcarbazole[7] and 4-alkoxybenzaldehyde[8] were prepared by the literature, which were purified by recrystallization from absolute ethanol and column chromatography (silica-gel, benzene-hexane). The results of the elemental analyses are given in Table I.

Measurements

Measurements of transition temperatures and microscopic observations of textures of mesophases were made using a Nikon polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. The absorption spectra were measured with a Hitachi 220 double beam UV-Visible spectrometer.

The typical experimental apparatus for measurements of photocurrents is illustrated in Figure 1.

A 500 W xenon lamp was used as a light source and the incident light was introduced to a Bausch & Lomb monochrometer grating 1200 grooves through a water filter. The light intensity was measured by an Eppley thermopile No. 22087, of which the electromotive force was detected by a microvoltmeter (Tokyo Riko). The incident light intensity at 400 nm was 1.0 mW/cm^2.

The sample cells used for measurements were of the sandwich type, consisting of two SnO_2-coated quartz glass plates and polyimide film as a spacer. The empty cell was set on the heating stage in a cryostat and the sample was injected into the cell space by capillarity at 150°C (the isotropic liquid state). Once the cell was cooled down to room temperature to crystallize the sample, the system was pumped down for about an hour and replaced with a dry nitrogen atmosphere.

A scheme for current-measurements is also illustrated in Figure 2, with a homogeneous alignment of rod-like molecules in a magnetic field. Currents were measured with a Takeda-riken electrometer, TR8651. The electric field was applied by dry batteries, which was detected by a Leader Electronics digital multimeter, LDM-853. All measurements in the nematic state were carried out for the homogeneous alignment of rod-like molecules caused by a magnetic field of 5 kG. This magnitude of the magnetic field was large enough to fully align the rod-like molecules to be homogeneous in the cell, since the saturation of the darkcurrent anisotropy was seen in a magnetic field of more than 4 kG.

The cryostat used for measurements was one with a built-in heating stage, on which the temperature could be controlled by a Chino digital-programmed temperature regulator (DP1110) with a thyristor

TABLE I

Results of elemental analysis of 2-(2-hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles

	Found/%			Required/%		
n	C	H	N	C	H	N
4	77.32	6.43	7.40	77.39	6.49	7.52
5	77.68	6.72	7.23	77.69	6.78	7.25
6	77.71	7.00	7.07	77.97	7.05	6.99
7	77.95	7.24	7.00	78.23	7.29	6.76
8	78.37	7.48	6.53	78.47	7.53	6.54
9	78.78	7.71	6.42	78.70	7.74	6.33
10	78.67	7.94	6.34	78.91	7.95	6.13
11	78.97	8.13	5.98	79.11	8.14	5.95
12	79.13	8.36	5.64	79.30	8.32	5.78
14	79.50	8.67	5.43	79.65	8.65	5.46

and the temperature was detected by a Cu-constantan thermocouple in conjunction with the regulator. The current was recorded by a Hitachi recorder, type 056.

The anisotropy of the dielectric constant of the pentyloxy compound, $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are dielectric constants along and perpendicular to the molecular long axis, respectively, was measured for a 25 μm-thick cell with an electrode area of 0.25 cm^2 in a magnetic field of 10 kG at 1 kHz (0.0395 V), using an Ando electric TR-10C capacitance bridge in conjunction with an equilibrium point detector, BDA-9, and a frequency transmitter, WBG-9.

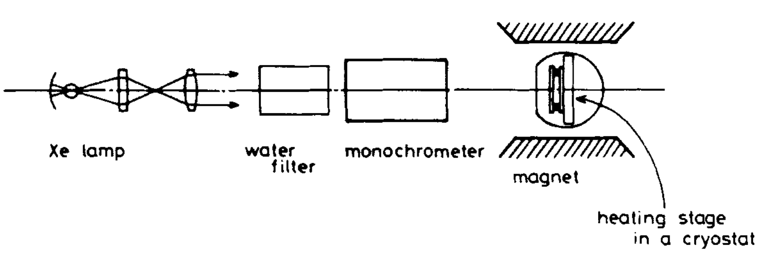


FIGURE 1 Schematic representation of the experimental apparatus.

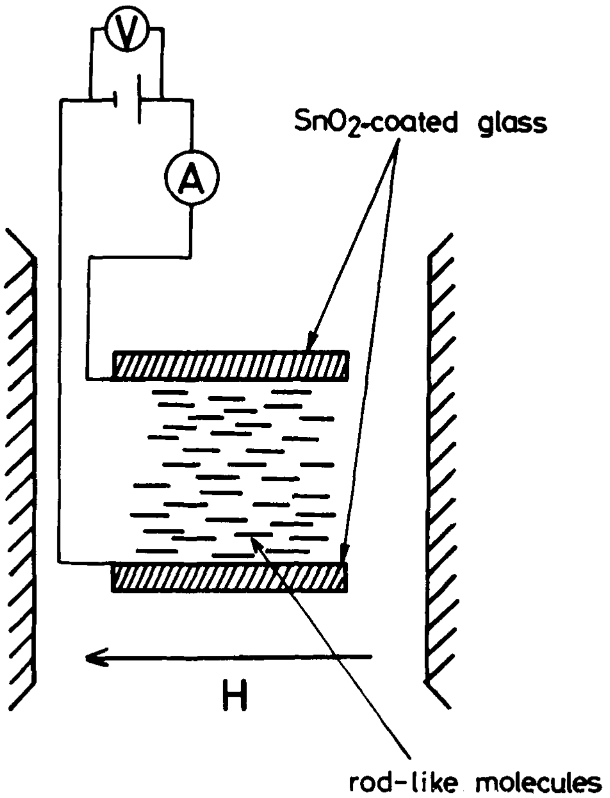


FIGURE 2 Schematic representation of the cell and the homogeneous alignment of rod-like molecules in a magnetic field.

RESULTS AND DISCUSSION

Mesomorphic properties

2-(2-Hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles exhibit a nematic phase in the butyloxy to tetradecyloxy compounds. The smectic A phase is shown for compounds with longer chain than nonyloxy one. The phase transition temperatures are listed in Table II.

Common trends of general rod-like liquid crystals appeared in this homologous series—that is, the odd-even alternations of the nematic to isotropic phase transition temperatures and the increase of the thermal stability of the smectic A phase (the smectic A to nematic phase transition temperatures) by elongation of the terminal chain.

9-Methylcarbazole has a bulky substituent attached to the nitrogen atom in the lateral direction and, therefore, a lower thermal stability

TABLE II

Transition temperatures (T/°C) of 2-(2-hydroxy-4-alkoxybenzylideneamino)-9-methylcarbazoles

n	T_{C-S_A} or N	T_{S_A-N}	T_{N-I}[a]
4	125.2		148.8
5	109.6		140.7
6	133.1		142.2
7	132.0		137.6
8	117.4		138.0
9	102.4	(85.0)[b]	136.0
10	108.5	(97.5)	134.0
11	94.5	110.5	131.3
12	108.1	115.5	129.6
14	110.0	124.7	128.5

[a] C: crystal, S_A: smectic A, N: nematic and I: isotropic.
[b] ( ): monotropic transition.

was seen as compared with the mesomorphic thermal stability of the isostructural liquid crystals containing dibenzofuran, dibenzothiophene or fluorene.[9] Though the bulkiness of the methyl group is considered to depress the formation of the smectic layer structure, the smectic A phase appears in the longer chain length ($n \geqq 9$). This situation is similar to that of fluorenone analogues.[10]

Photoconducting behavior

A pentyloxy compound was selected for the photoconductive measurements.

The symmetrical sandwich-type cell exhibited a photo-response in the region where the molecules absorb photons. Moreover, the photoresponse was found even in the longer wavelength region where the molecule does not seem to have light-absorption, though the response was small. Figure 3 shows the absorption and action spectra in the nematic state (120°C). No differences of the action spectra appeared between the positive and the negative electrode illuminations on the whole, except for the magnitude of the photocurrent. The photocurrent for a positive electrode illumination is larger than that for a negative one.

The action spectrum in the nematic state was found to coincide with the absorption spectrum of a film in shape in a longer wavelength region than 360 nm. However, the coincidence was not seen in the shorter wavelength region. This seems to be due to light absorption of the electrode material, SnO_2 itself.

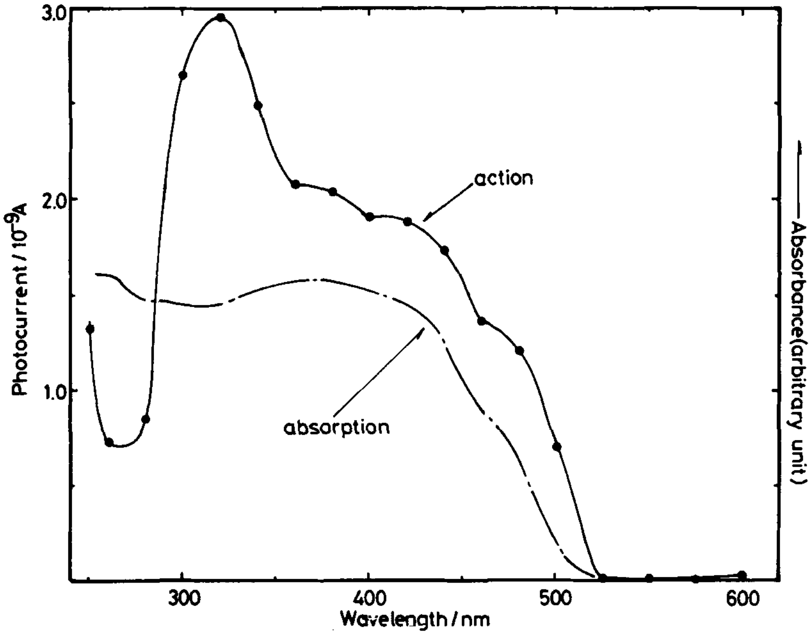


FIGURE 3 Absorption and action spectra for a film of 2-(2-hydroxy-4-pentyloxy-benzylideneamino)-9-methylcarbazole in the nematic state (120°C). The action spectrum is for that at zero bias.

On the other hand, the light exponent σ was obtained to be 0.56 from plots of photocurrent against the incident light intensity which appeared to have a good linearity, as shown in Figure 4. This value and the coincidence of the action spectrum with the absorption one indicate that the charge carrier generation is caused by way of an extrinsic mechanism in the presence of recombination.[11]

This extrinsic process could be supported by the fact that the photoelectromotive force and photocurrent at zero bias are exhibited. This result also indicates that the SnO_2-liquid crystals interface is photoactive, and considering the fact that the photocurrent increases as oxygen is introduced into the cryostat, the photocurrent is inferred to be caused by the interaction among SnO_2, O_2 and the liquid crystalline molecules.

Figure 5 shows the temperature dependence of the dark- and the photo-currents. The behavior following the Arrhenius' equation was seen for both the dark- and the photo-currents. The conductivities of the crystalline, nematic and isotropic liquid phases are in the order of less than 10^{-12}, 10^{-10} and 10^{-9} Scm^{-1}, respectively. The activation

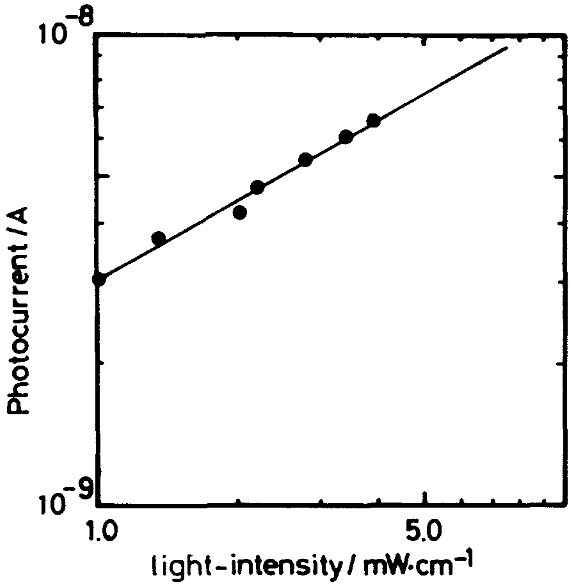


FIGURE 4 A plot of the photocurrent vs. incident light intensity at 400 nm under 20.8 V cm^{-1}.

energies for conduction were calculated to be 0.36 and 0.56 eV for the isotropic and the nematic phases, respectively. The darkcurrent is shown to drastically increase at the crystal to nematic phase transition.

On the other hand, the photocurrent also exhibits a large increase at the crystal to nematic transition. However, the magnitude of the photocurrent in the phases with fluidity is smaller than that of the darkcurrent by about one order, while in the crystalline phase, the difference appears to be small. The activation energies for photoconduction in the positive electrode illumination were calculated to be 0.17 and 0.19 eV for the isotropic and nematic phases, respectively. The difference of the activation energies between the dark- and the photo-currents implies that the carrier species which contributed to the photocurrent are different from those which contributed to the darkcurrent. Furthermore, the sudden decrease of the photocurrent is seen near the crystal to nematic transition on the heating run, which seems to be caused by pretransitional phenomena.

The temperature dependence of the photoelectromotive force shows the inverse case against that of the photocurrent—that is, the photoinduced voltage decreases as the temperature is elevated through the crystalline, nematic and isotropic phases. The sign of the illuminated

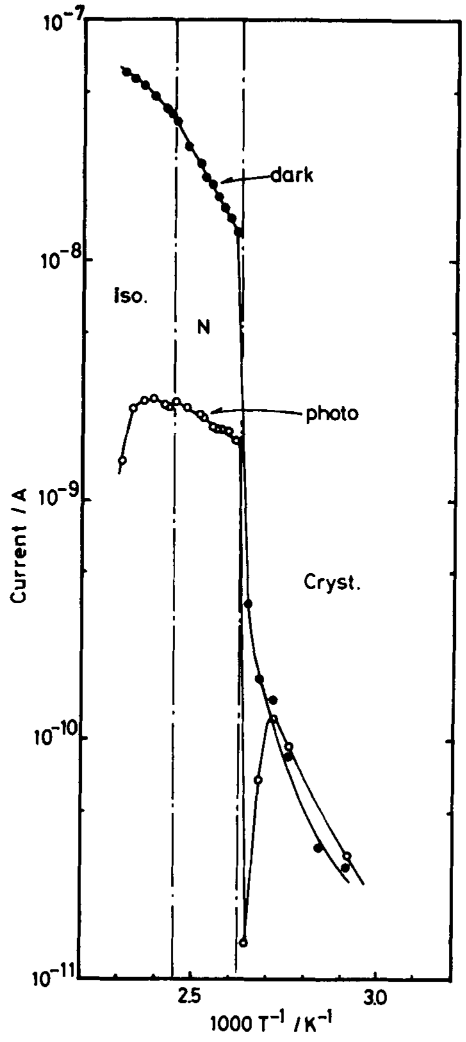


FIGURE 5 Temperature dependence of the dark- and the photo-currents for a film of 2-(2-hydroxy-4-pentyloxybenzylideneamino)-9-methylcarbazole. The photocurrent is for the positive electrode illumination under 20.8 V cm^{-1}.

electrode appeared to be positive at zero bias, which is ascertained by the fact that the photocurrent increases in addition to the dark-current when the positive electrode is illuminated, but the negative electrode illumination decreases the darkcurrent. In an extreme case where the applied voltage is very small and the incident light intensity is large enough, the direction of current is reversed.

Figure 6 shows the current-voltage characteristics for the nematic state, where the darkcurrent appeared to be ohmic in the range of less than 600 V cm^{-1}, and the photocurrent once increases and next decreases followed by increasing again as the field strength rises. This situation rather resembles negative resistance. In the case of the negative electrode illumination, also such a situation appeared, but in the range of 0–200 V cm^{-1}, a rectification behavior was exhibited, implying that the excitons of the molecules could interact with the bands of SnO_2 since such a rectification was not found in the darkcurrent behavior.

It is known, however, that the rod-like liquid crystals of *n*-type exhibit a dynamic scattering mode beyond the threshold voltage.[12] This 9-methylcarbazole liquid crystal is of negative type, of which the dielectric anisotropy was measured to be −1.0 at 120°C. By microscopic observations, the molecules align homogeneously on the coated SnO_2 film and the Williams domain was formed over a direct voltage of 3.84 V (1536 V cm^{-1}). Thus, the range exhibiting the behavior like a negative resistance for this liquid crystal is not considered to be contained in the range in which the Williams domain occurs, meaning that the apparent negative resistance is not due to the molecular random flow by the applied field.

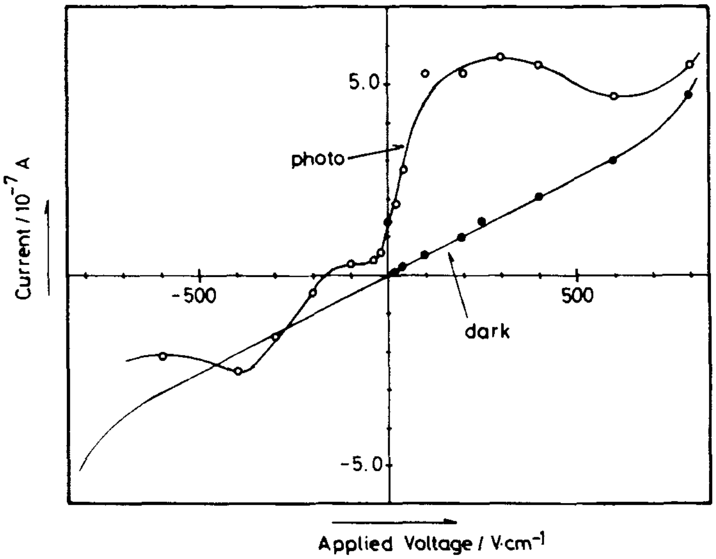


FIGURE 6 Current-voltage characteristics for a film of 2-(2-hydroxy-4-pentyloxybenzylideneamino)-9-methylcarbazole in the nematic state (120°C). The incident light was of 400 nm.

This consideration was also supported by the current-voltage characteristics for the isotropic liquid phase, as shown in Figure 7. The negative resistance was apparently exhibited even in the isotropic

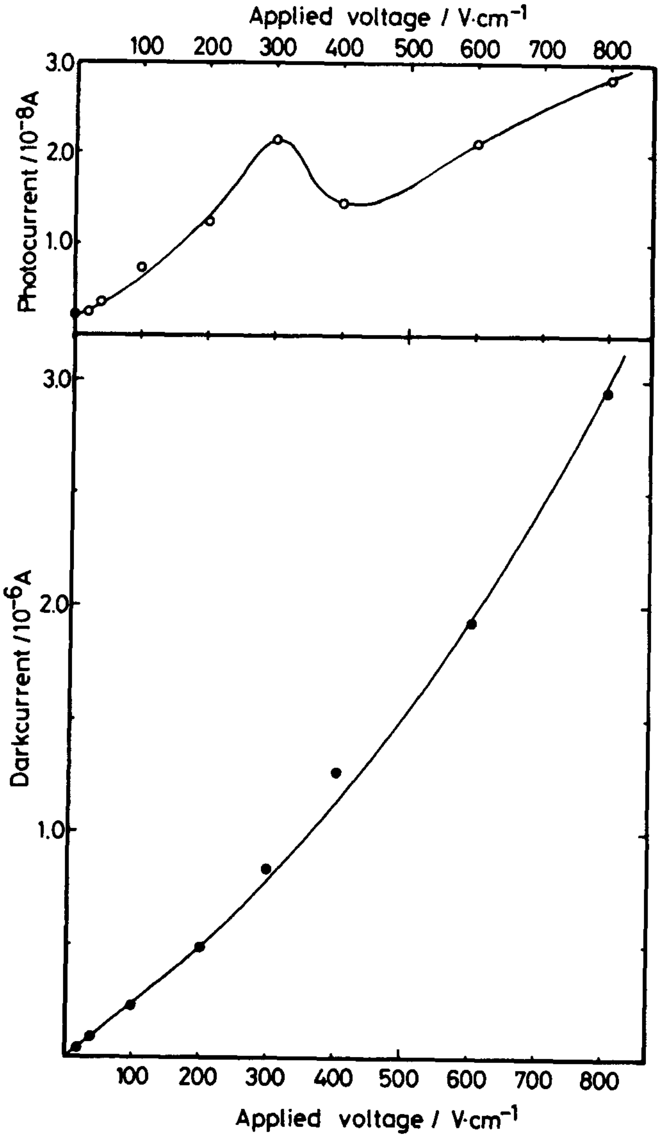


FIGURE 7 Current-voltage characteristics for a film of 2-(2-hydroxy-4-pentyloxybenzylideneamino)-9-methylcarbazole in the isotropic liquid state (145°C). The incident light was of 400 nm.

liquid phase, though the maximum and minimum points appeared at a different field strength from that in the nematic phase.

On the other hand, the current-voltage characteristics for the crystalline phase showed a different behavior. The photocurrent changes little as the field strength is elevated up to 40000 V cm^{-1}, while the darkcurrent increases, as seen in Figure 8.

These results indicate that though the applied field might assist the charge carrier generation, it becomes more difficult for the carriers to move in a bulk region in the crystalline state than in the fluid states. This seems to lead to a larger photocurrent in the fluid states and to the large contribution of the ionic carrier transport mechanism to the photocurrent. However, the electronic transport also seems to

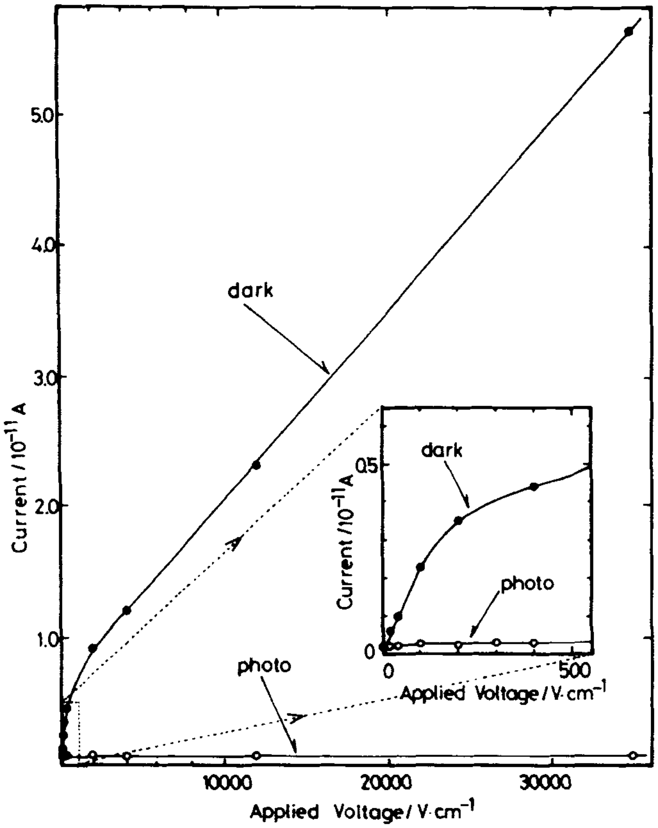


FIGURE 8 Current-voltage characteristics for a film of 2-(2-hydroxy-4-pentyloxybenzylideneamino)-9-methylcarbazole in the crystalline state (28.5°C). The incident light was of 400 nm.

contribute to the photocurrent, considering the complex transport mechanism of liquid pyrene which consists of a mixture of ionic motion and phonon-assisted electron transfers.[13]

It seems that the proposition by K. Okamoto et al.[2] could be applied to this case, meaning that the carrier species are ionic and that the negative carrier is $O_2^{\bar{\cdot}}$ derived from oxygen molecules contained in the system and the positive carrier is cation radicals of 9-methylcarbazole liquid crystals. And the photoconducting behavior in the nematic state resembles that in the isotropic state rather than that in the crystalline state.

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