Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Highly photoconductive discotic liquid crystals Structure-property relations in the homologous series of hexa-alkoxytriphenylenes

H. Bengs[a]; F. Closs[b]; T. Frey[c]; D. Funhoff[c]; H. Ringsdorf[a]; K. Siemensmeyer[b]
[a] Universität Mainz, Institut für Organische Chemie, Mainz, Germany [b] BASF AG, Farbenlaboratorium, 67056, Ludwigshafen, Germany [c] BASF AG, Kunststofflaboratorium, 67056, Ludwigshafen, Germany

To cite this Article Bengs, H. , Closs, F. , Frey, T. , Funhoff, D. , Ringsdorf, H. and Siemensmeyer, K.(1993) 'Highly photoconductive discotic liquid crystals Structure-property relations in the homologous series of hexa-alkoxytriphenylenes', Liquid Crystals, 15: 5, 565 — 574

To link to this Article: DOI: 10.1080/02678299308036478

URL: http://dx.doi.org/10.1080/02678299308036478

LIQUID CRYSTALS, 1993, VOL. 15, NO. 5, 565–574

Highly photoconductive discotic liquid crystals

Structure–property relations in the homologous series of hexa-alkoxytriphenylenes

by H. BENGS§, F. CLOSS†, T. FREY‡, D. FUNHOFF‡*,
H. RINGSDORF*§ and K. SIEMENSMEYER†

† BASF AG, Farbenlaboratorium, 67056 Ludwigshafen, Germany
‡ BASF AG, Kunststofflaboratorium, 67056 Ludwigshafen, Germany
§ Universität Mainz, Institut für Organische Chemie,
J. J. Becher-Weg 18-20, 55099 Mainz, Germany

(Received 6 May 1993; accepted 25 June 1993)

Four discotic liquid crystals (LCs) from the hexa-alkoxytriphenylene series ($R = C_nH_{2n+1}$, $n = 5, 7, 9, 11$) classified as D_{ho} phases were investigated with respect to their photoconducting properties. Under irradiation, all samples show photoconductivity within the mesophase, whereas in the isotropic phase the photocurrent drops to zero. All of the observed effects, the phase dependence of the photocurrent, the increasing values of the photocurrent with decreasing length of the side chains, and the higher photoconductivity during the cooling process, can be explained in terms of the transition temperatures, the intercolumnar distances and the orientation behaviour. Comparison of the photocurrents of the investigated homologues at a reduced temperature leads to an activation energy of 0·67 eV for the charge transport.

1. Introduction

Molecules generating discotic liquid crystalline phases usually consist of a flat aromatic core surrounded by several aliphatic side chains. Their structure corresponds in most cases to a columnar packing of the rigid cores. The columns themselves organize in a two dimensional superlattice as for instance a hexagonal one. Hexa-alkoxytriphenylenes are well-known representatives of this class of liquid crystals (LCs) (see figure 1) [1–5].

As a result of the columnar arrangement, discotic LCs have a preferred direction along the axis of the columns. The distance between two discs within the columns is

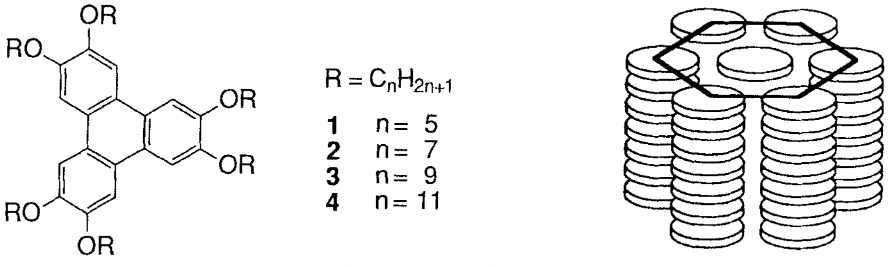


Figure 1. Formulae for 2,3,6,7,10,11-hexa-alkoxytriphenylenes **1**–**4** ($R = C_nH_{2n+1}$; $n = 5,7,9,11$) and a schematic presentation of a D_{ho} phase (discotic hexagonal ordered).

---

* Authors for correspondence.

3–4 Å, whereas the intercolumnar distance, dependent on the size and length of the substituents, amounts to more than 18 Å. This packing behaviour of discotic LCs provides opportunities for the study of one dimensional transport processes such as energy migration [6, 7], electrical conductivity [8–15] and photoconductivity [16–18].

Photoconductivity measurements have been used to determine phase transition temperatures in LCs for more than two decades [19]. The idea of using the orientability of LCs for enhancing charge carrier mobilities was first discussed in the eighties, e.g. for doped liquid crystalline matrices [20], and low molar mass calamitic [21] and discotic [22, 2?], as well as polymeric thermotropic [24] and lyotropic LCs [25].

Recently, a high charge carrier mobility in the discotic columnar phase of hexapentoxytriphenylene was reported [17]; for the first time non-dispersive charge carrier transport in LCs was observed. The present paper deals with the photoconductivity of the homologous series of discotic liquid crystalline hexa-alkoxytriphenylenes **1–4** (see figure 1).

2. Experimental

2.1. *Synthesis*

The lower homologues **1** and **2** (C_nH_{2n+1}, $n=5$ and 7) were synthesized according to the literature [26] by trimerization of *o*-dialkoxybenzenes in H_2SO_4 (70 per cent) with $FeCl_3$ as the oxidizing agent. The higher homologues **3** and **4** (C_nH_{2n+1}, $n=9$ and 11) were obtained with 2,3,6,7,10,11-triphenylenehexayl hexa-acetate [27] as the starting material in a sixfold etherification by phase transfer catalysis as described below for 2,3,6,7,10,11-hexanonoxyphenylene **3**: 1 g (1·7 mmol) of 2,3,6,7,10,11-triphenylenehexayl hexa-acetate, 1 g (3·7 mmol) of 18-crown-6, 3·6 g (17·4 mmol) of nonyl bromide, 1 g (17·9 mmol) of KOH pellets and 10 ml of dried toluene were mixed together and stirred in a closed reaction vessel for two hours at 60°C. Completion of the reaction was checked by thin layer chromotagraphy. The reaction mixture was washed with water, 0·5 N H_2SO_4, saturated NaCl solution and dried over $MgSO_4$. The organic solvent and the unreacted alkylation agent were removed under reduced pressure at a maximum temperature of 60°C. The crude residue was purified twice by flash chromatography with a mixture of CH_2Cl_2 and light petroleum as eluent (vol. ratio = 2 : 1). Final recrystallization from ethanol/hexane (vol. ratio = 1 : 1) resulted in 900 mg (0·8 mmol) of white product **3** (Yield: 48 per cent). The purity of all hexa-alkoxytriphenylenes **1–4** was checked by thin layer chromatography. Elemental analysis and ^1H N.M.R. data were in accordance with the given structures.

Table 1. Phase transition temperatures for the hexa-alkoxytriphenylenes **1–4** [1–3].

Compound	Alkyl chain length C_nH_{2n+1} n	Phase behaviour† °C
1	5	C 69 D_{ho} 122 I
2	7	C 68·6 D_{ho} 93 I
3	9	C 57 D_{ho} 77·6 I
4	11	C 54 D_{ho} 66 I

† C = crystalline phase, D_{ho} = discotic hexagonal ordered phase, I = isotropic phase.

Table 2. Structural data for the hexa-alkoxytriphenylenes **1**–**4**: inter and intra-molecular distances, the calculated areas covered by one molecule and the percentage area of the triphenylene core.

Compound	Alkyl chain lengh C_nH_{2n+1} n	d_{inter}† Å	d_{intra}‡ Å	A§ Å^2	$A_{\%}$‖ Å^2
1	5	20·19	3·60	319	58·6
2	7	22·55	3·61	399	46·8
3	9	24·26	3·59	462	40·5
4	11	26·13	3·59	535	35·0

† Intercolumnar distance as determined by X-ray [28].

‡ Intracolumnar distance as determined by X-ray [28].

§ Calculated area covered by one molecule, approximated as a circle, on the basis of the X-ray data.

‖ Percentage area of the triphenylene core based upon the extrapolated value for $n = 0$ (187 Å^2).

2.2. *Characterization*

The optical determination of the phase behaviour was done with a Leitz polarizing microscope Ortholux II Pol connected with a Mettler hot stage FP 80/82. The measured transition temperatures are in agreement with the literature and are given in table 1 [1–3]. The intercolumnar distances given in table 2 were measured by wide angle X-ray for the liquid crystalline phase 10–25°C below the clearing temperature [28].

2.3. *Photoconductivity measurements*

For the measurements of the photocurrent, the sample was placed between two glass plates coated with transparent indium tin oxide (ITO) as electrode material. The distance between the plates was adjusted to about 10 μm by a Mylar® foil. The area of the electrode was about 4 mm^2. A DC voltage of 9 V was applied to the cell, which corresponds to an electric field of 900 kV m^{-1}. The sample was illuminated by a chopped halogen light (frequency: 10 Hz) focused on the plane of the sample. The detection of the photocurrent was performed by measuring the voltage drop over a resistance of 10 kΩ with a lock-in-amplifier (Princeton Applied Research, EG&G 5210). The temperature of the sample was controlled through a modified Mettler FP 80/82 hot stage. The heating rate during the measurements of the photocurrent was adjusted to 0·5°C min^{-1}.

3. Results and discussion

Although photoconductive properties of disc-like systems have been described before [22, 23], highly photoconductive hexa-pentoxytriphenylenes were reported only recently [17, 18]. The interesting point is that only in the liquid crystalline phase is the detection of a photocurrent possible (see figure 2, heating curve and table 1): the photocurrent increases rapidly at the phase transition from the crystalline to the discotic hexagonal phase (C/D_{ho}), levels off upon further increase in temperature, reaches its maximum a few degrees below the transition from the discotic to the isotropic phase (D_{ho}/I) and collapses at the phase transition D_{ho}/I. This temperature

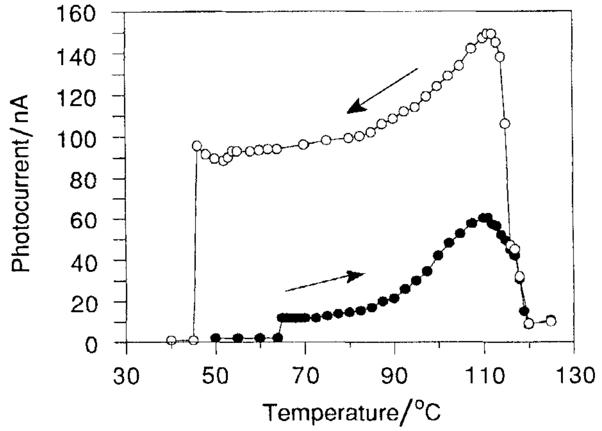


Figure 2. Photocurrent of hexapentoxytriphenylene **1** ($R = C_5H_{11}$) and its dependence upon temperature: (●), heating curve; (○), cooling curve.

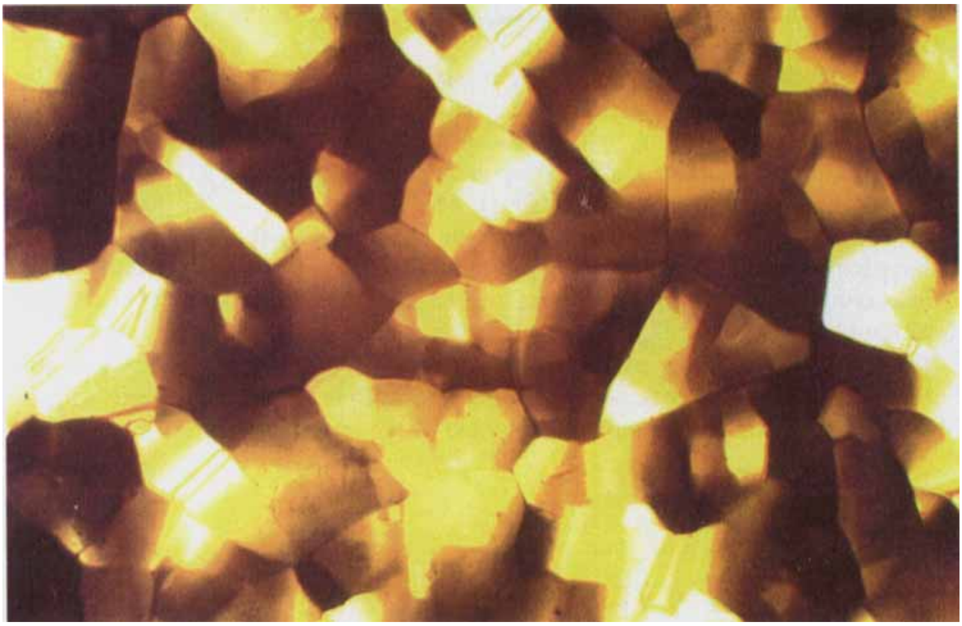
dependence of the photoconducting behaviour within the liquid crystalline phase can be understood if two effects determining the photoconductivity are taken into account:

(i) an exponential increase in conductivity with temperature, and
(ii) the influence of the degree of orientation (the order parameter) on the conductivity.

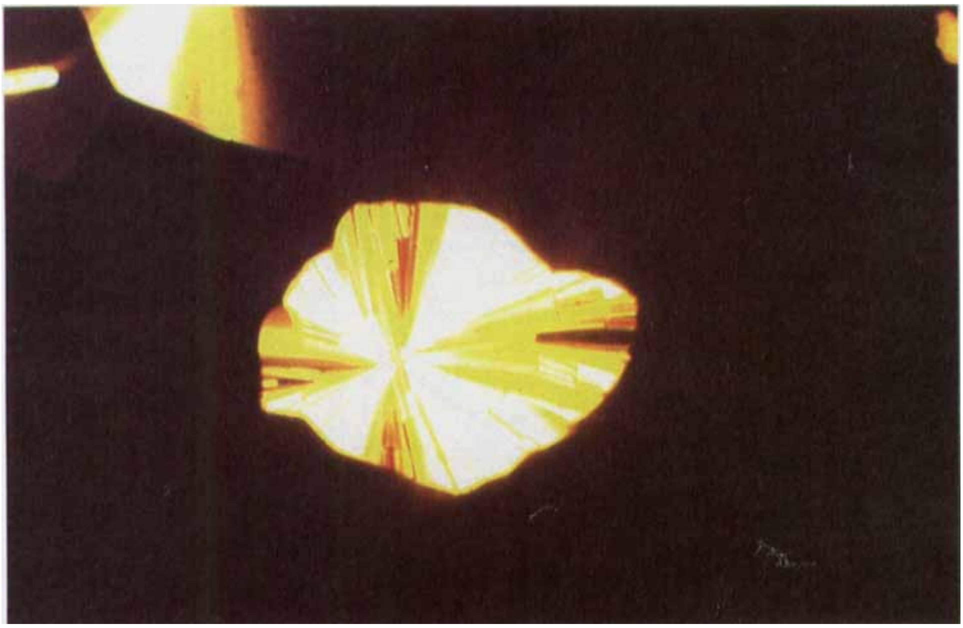
Qualitatively, the temperature dependence of the photocurrent is the same during the heating and cooling cycle (see figure 2). During the cooling process (see figure 2, cooling curve), only the transition temperatures between the phases are shifted slightly to lower temperatures because of the well-known supercooling effect. Quantitatively, however, the photocurrent observed is considerably higher while cooling the sample from the isotropic phase as compared to heating it from the crystalline state.

This can be explained by the fact that, while cooling the sample from the isotropic phase, an orientation effect takes place. Microscopic observations reveal that the homeotropic alignment of the director $\vec{n}$ becomes much better on cooling. This arrangement of the columns perpendicular to the surface results in an increased number of dark areas as observed microscopically using crossed polarizers (figure 3, e.g. **1**). This observation points to the fact that the higher photocurrent during the cooling cycle originates in the better orientation of the liquid crystalline phase. This better orientation may result either in a reduction in the number of defects in the mesophase which otherwise would act as traps for the charge carriers or a larger number of charge transporting columns of hexa-alkoxytriphenylenes oriented properly or both.

The temperature dependence of the photocurrent for the other triphenylene derivatives **2**–**4** (C_nH_{2n+1}, $n = 7, 9, 11$) differs only slightly from that for the pentyl derivative **1** (see figure 4). All the homologues, except the nonyl derivative **3**, exhibit a jump in the photocurrent at the phase transition C/D_{ho} and a break down at the clearing temperature (D_{ho}/I, cf. table 1). As already described for compound **1** (see figure 2), during the cooling process, supercooling effects can be observed, as well as higher photocurrents compared to the heating run. For the highest homologue **4**, for example, only the better orientation present during the cooling cycle leads to a measurable



(*a*)



(*b*)

Figure 3. Photomicrographs of hexa-pentoxytriphenylene **1** ($R = C_5H_{11}$) within the mesophase range, as observed using crossed polarizers: (*a*) during heating from the crystalline phase at 118°C, (*b*) during cooling from the isotropic phase at 117°C.

current (see figure 4). In contrast to all other investigated triphenylenes, the nonyl derivative **3** exhibits a different temperature dependence of the photocurrent (see figure 4).

At a temperature of 40°C, i.e. in the crystalline state, the photocurrent has the highest level of about 10 nA and decreases up to a temperature of about 48°C (see figure 4(*a*)). Upon further heating, two steps in the temperature dependence of the photocurrent were observed: The first drop in the photocurrent at 56°C is related to the melting of the sample [1–3] (see table 1). The second drop in the photocurrent corresponds to the clearing temperature. In the D_{ho} phase, from about 56°C to 74°C, the same temperature dependence is found as for the pentyl **1** and heptyl **2** derivatives, i.e. increasing photocurrent with increasing temperature and a drop at the phase transition to the isotropic fluid.

The unusual behaviour of the nonyl derivative **3**, namely the increase in the photocurrent at the discotic to crystalline transition, is not consistent with a polycrystalline phase and cannot be explained at the moment.

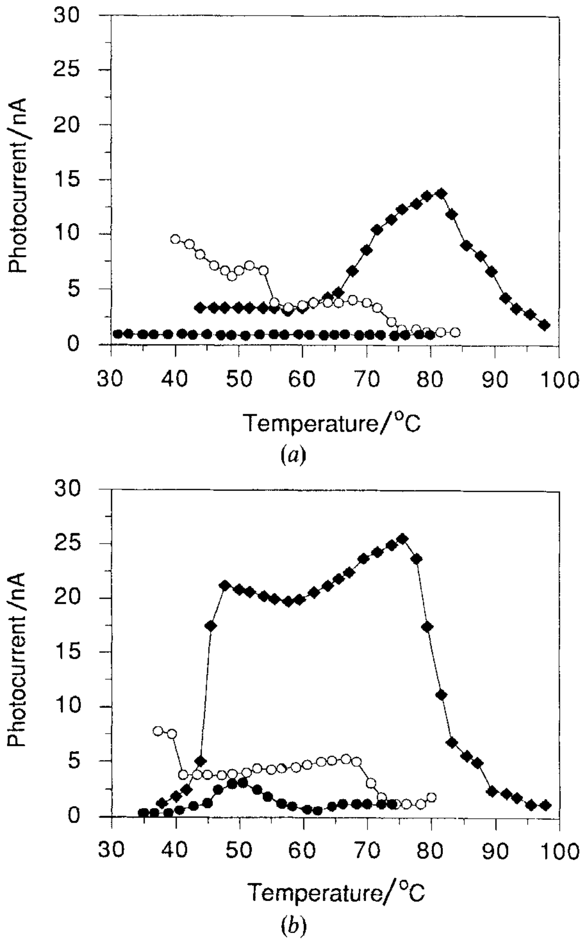


Figure 4. Photocurrents of the hexa-alkoxytriphenylenes **2** (◆), **3** (○), and **4** (●), in relation to temperature: (*a*) heating and (*b*) cooling curves.

Comparing the photoconductivity of the four triphenylene derivatives (see figures 2 and 4), the most prominent feature is the dramatic decrease in the photocurrent with increasing chain length of the alkoxy units. Plotting the photocurrent at 10 K below the clearing temperature against the number of carbon atoms in the side chain, one can observe a nearly exponential decrease (figure 5). This effect may be explained by the different molecular packings of the derivatives. In general, inter and intra-molecular distances for discotic LCs vary with the side chain length and should be taken into account in the interpretation of the results. Although a strong influence of any change in the intracolumnar distances on the conducting behaviour is expected (by altering the orbital overlap), this argument can be neglected. As shown in table 2, the intracolumnar distances are identical within experimental error for all four triphenylene derivatives **1–4** and therefore cannot explain the differences in the photocurrent within the mesophase (see figures 2 and 4). As opposed to this, the intercolumnar distances in the

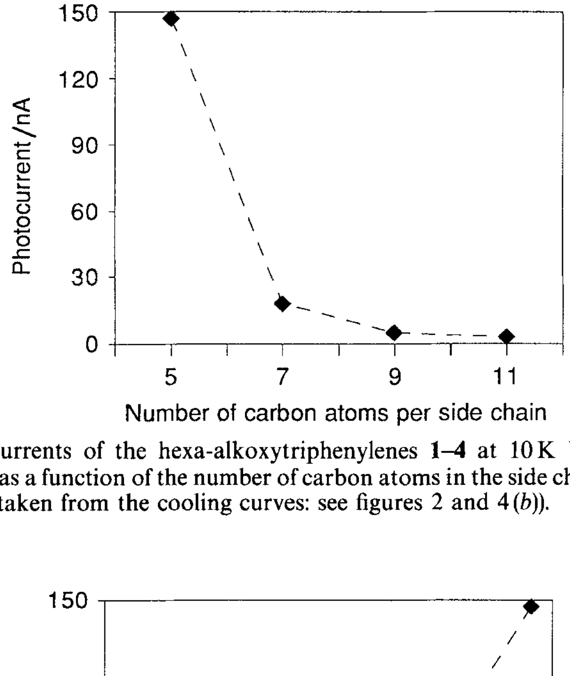


Figure 5. Photocurrents of the hexa-alkoxytriphenylenes **1–4** at 10 K below the clearing temperature as a function of the number of carbon atoms in the side chains (photocurrent values were taken from the cooling curves: see figures 2 and 4(*b*)).

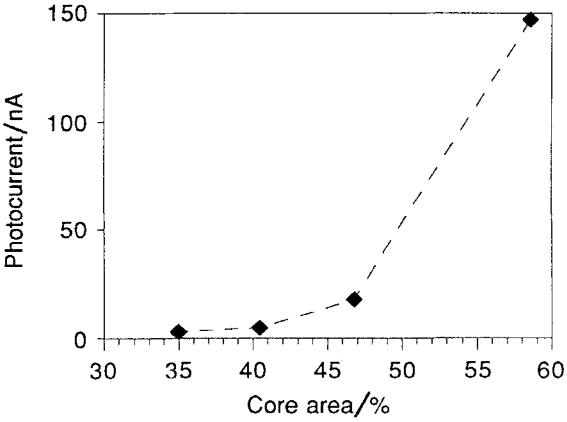


Figure 6. Photocurrents of the hexa-alkoxytriphenylenes **1–4** at 10 K below the clearing temperature as a function of the percentage area $A_{\%}$ of the triphenylene core (photocurrent values were taken from the cooling curves: see figures 2 and 4(*b*)).

mesophase increase from 20 Å to 26 Å with increasing chain length from the pentyl **1** to the undecyl derivative **4** (cf. table 2). Simultaneously with this increase, the photocurrent decreases. In conclusion, only the triphenylene core is responsible for the photoconducting properties. As a result of the increasing intercolumnar distances, the area covered by the triphenylene core is strongly reduced (table 2, column $A_{\%}$). Figure 6 shows the photocurrent at a temperature 10 K below the transition D_{ho}/I plotted against the percentage of the area covered by the triphenylene cores. In this plot, the absolute temperature for each derivative is different. This may explain the nearly exponential decrease in the photocurrent with increasing chain length (cf. figure 5).

The temperature dependence of the photocurrent and the strong influence of the alkyl chain length on the photocurrent within the homologous series can be explained by taking into account that the photocurrent (I_{ph}) is influenced by three major effects:

(i) the temperature dependence of the order parameter $S(T)$,
(ii) the area covered by the triphenylene core $A_{\%}$, and
(iii) the charge transport thermally induced with an activation energy E_a.

Assuming Arrhenius-type behaviour, the photocurrent can be described as

$$I_{ph}=I_o\cdot A_{\%}\cdot S(T)\cdot\exp(-E_a/RT), \tag{1}$$

with the proportionality coefficient I_o.

For a derivative **X**, the photocurrent at a temperature 10 K below the clearing temperature (T_{cl}) equation (1) can be transformed

$$I_{ph}(\mathbf{X})=I_0\cdot A_{\%}(\mathbf{X})\cdot S(T_{cl}(\mathbf{X})-10)\cdot\exp[-E_a/R\cdot(T_{cl}(\mathbf{X})-10)]. \tag{2}$$

where $A_{\%}(\mathbf{X})$ and $T_{cl}(\mathbf{X})$ are the area covered by the triphenylene core and the clearing temperature, respectively. A simplified expression can be obtained by considering the ratio of the photocurrent of two derivatives, using compound **4**, the highest investigated homologue, as a reference. This results in equation 3

$$\frac{I_{ph}(\mathbf{X})}{I_{ph}(\mathbf{4})}=\frac{I_0\cdot A_{\%}(\mathbf{X})\cdot S(T_{cl}(\mathbf{X})-10)\cdot\exp[-E_a/R\cdot(T_{cl}(\mathbf{X})-10)]}{I_0\cdot A_{\%}(\mathbf{4})\cdot S(T_{cl}(\mathbf{4})-10)\cdot\exp[-E_a/R\cdot(T_{cl}(\mathbf{4})-10)]}. \tag{3}$$

Three more assumptions lead to a further simplification of equation (3):

(i) because only the triphenylene core is photoconductive, the charge transport mechanism and the efficiency of charge generation in the homologous series of hexa-alkoxytriphenylenes is assumed to be the same. Therefore the proportionality coefficient I_0 is a constant for all hexa-alkoxytriphenylenes,
(ii) the nature of intrinsic traps arising in the liquid crystalline structure are supposed to be equal. Consequently the activation energy E_a for the four derivatives is the same,
(iii) at a temperature 10 K below the clearing temperature (T_{cl}), the order parameter $S(T_{cl}(\mathbf{X})-10)$ is the same for the four triphenylene derivatives **1**–**4**.

Thus equation (4) is obtained

$$\ln\left(\frac{I_{ph}(\mathbf{X})/A_{\%}(\mathbf{X})}{I_{ph}(\mathbf{4})/A_{\%}(\mathbf{4})}\right)=\frac{E_a}{R}\cdot\frac{T_{cl}(\mathbf{X})-T_{cl}(\mathbf{4})}{(T_{cl}(\mathbf{X})-10)\cdot(T_{cl}(\mathbf{4})-10)}. \tag{4}$$

With equation (4) it is possible to determine the activation energy E_a for the charge transport process. In figure 7 the plot according to equation (4) with the measured

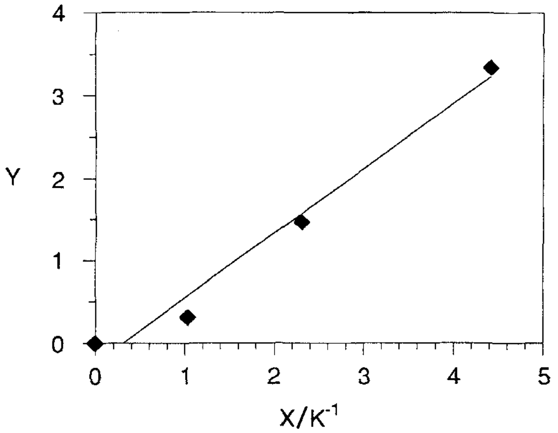


Figure 7. Determination of the activation energy E_a in accordance with equation (4) (photocurrent values were taken from the cooling curves: see figures 2 and 4 (*b*)): $Y = \ln[I_{ph}(\mathbf{X}) \cdot A_{\%}(\mathbf{4}) / I_{ph}(\mathbf{4}) \cdot A_{\%}(\mathbf{X})]$, and $X = [T_{cl}(\mathbf{X}) - T_{cl}(\mathbf{4})] / [(T_{cl}(\mathbf{X}) - 10) \cdot (T_{cl}(\mathbf{4}) - 10)] \cdot 10^4$. Linear regression: $Y = 7\,863X - 0{\cdot}245$, $r = 0{\cdot}989$.

values of the cooling curves in figures 2 and 4 (*b*) is given. As expected a linear behaviour is observed. The activation energy estimated is 65 kJ mol^{-1} or 0·67 eV per molecule. This is in good accord with the value of 0·6 eV obtained for hexa-pentoxytriphenylene by the time-of-flight method [17], and with activation energies of 0·4 eV to 0·7 eV obtained for other well-known photoconductors (e.g. polyvinylcarbazole) [29, 30].

4. Conclusions

In this paper, the photoconductivity of hexa-alkoxytriphenylenes, as typical representatives of discotic LCs forming hexagonal columnar mesophases, was investigated. Measurements of the dependence of the photocurrent on temperature reveal sharp drops at the phase transition D_{ho}/I for all four homologues examined. In all cases, higher photocurrents within the discotic columnar mesophase was observed. The main results can be summarized as follows:

(i) the increase in the photocurrent in the mesophase with increasing temperature is determined by a thermally induced increase in the conductivity and by the order parameter,
(ii) the higher photocurrent during the cooling cycle is attributed to a better orientation of the discotic LC,
(iii) the intensity of the photocurrent is mainly determined by the area covered by the triphenylene core.

The financial support by the Bundesministerium für Forschung und Technologie (BMFT Projektnummer 03 M 4035 0) is gratefully acknowledged. The authors are indebted to Dipl. Phys. J. Wendling (TH Darmstadt) for collecting the X-ray data.

References

[1] Destrade, C., Mondon, M. C., and Malthête, J., 1979, *J. Phys., Paris*, **40**, C3-17.
[2] Destrade, C., Huu Tinh, N., Gasparoux, H., Malthête, J., and Levelut, A. M., 1981, *Molec. Crystals liq. Crystals*, **71**, 111.
[3] Levelut, A. M., 1979, *J. Phys., Paris*, **40**, L-81.

[4] CHANDRASEKHAR, S., and RANGANATH, G. S., 1990, *Rep. Prog. Phys.*, **53**, 57.

[5] BENGS, H., EBERT, M., KARTHAUS, O., KOHNE, B., PRAEFCKE, K., RINGSDORF, H., WENDORFF, J. H., and WÜSTEFELD, R., 1990, *Adv. Mater.*, **2**, 141.

[6] MARKOVITSI, D., LÉCUYER, I., and SIMON, J., 1991, *J. phys. Chem.*, **95**, 2752.

[7] MARKOVITSI, D., LÉCUYER, I., LIANOS, P., and MALTHÊTE, J., 1991, *J. chem. Soc. Faraday Trans.*, **87**, 1785.

[8] SAEVA, F. D., REYNOLDS, G. A., and KASZCZUK, L., 1982, *J. Am. chem. Soc.*, **104**, 3524.

[9] PIECHOCKI, C., SIMON, J., SKOULIOS, A., GUILLON, D., and WEBER, P., 1982. *J. Am. chem. Soc.*, **104**, 5245.

[10] STRZELECKA, H., GIONIS, V., RIVORY, J., and FLANDROIS, S., 1983, *J. Phys., Paris*, **44**, C3-1201.

[11] CHIANG, L. Y., STOKES, J. P., SAFINYA, C. R., and BLOCH, A. N., 1985, *Molec. Crystals liq. Crystals*, **125**, 279.

[12] KORMANN, R., ZUPPIROLI, L., GIONIS, V., and STRZELECKA, H., 1986, *Molec. Crystals liq. Crystals*, **133**, 283.

[13] VON KEULEN, J., WARMERDAM, T. W., NOLTE, R. J., and DRENTH, W., 1987, *Recl Trav. chim. Pays-Bas Belg.*, **106**, 534.

[14] BODEN, N., BUSHBY, R. J., CLEMENTS, J., JESUDASON, M. V., KNOWLES, P. F., and WILLIAMS, G., 1988, *Chem. Phys. Lett.*, **152**, 94.

[15] SCHOUTEN, P. G., WARMAN, J. M., DE HAAS, M. P., FOX, M. A., and PAN, H.-L., 1991, *Nature, Lond.*, **353**, 736.

[16] CATRY, C., VAN DER AUWERAER, M., DE SCHRYVER, F. C., BENGS, H., KARTHAUS, O., HÄUßLING, L., and RINGSDORF, H., 1993, *Makromolek. Chem.* (in the press).

[17] ADAM, D., CLOSS, F., FREY, T., FUNHOFF, D., HAARER, D., RINGSDORF, H., SCHUHMACHER, P., and SIEMENSMEYER, K., 1993, *Phys. Rev. Lett.*, **70**, 457.

[18] CLOSS, F., SIEMENSMEYER, K., FREY, T., and FUNHOFF, D., 1993, *Liq. Crystals*, **14**, 629.

[19] KUSABAYASHI, S., and LABES, M. M., 1969, *Molec. Crystals liq. Crystals*, **7**, 395.

[20] CHAPOY, L. L., MUNCK, D. K., RASMUSSEN, K. H., JUUL DIEKMANN, E., SETHI, R. K., and BIDDLE, D., 1984, *Molec. Crystals liq. Crystals*, **105**, 353.

[21] SHIMIZU, Y., SHIGETA, K., and KUSABAYASHI, S., 1986, *Molec. Crystals liq. Crystals*, **140**, 105.

[22] SHIMIZU, Y., ISHIKAWA, A., and KUSABAYASHI, S., 1986, *Chemistry Lett.*, 1041.

[23] SHIMIZU, Y., MIYA, M., NAGATA, A., OHTA, H., MATSUMURA, A., YAMAMOTO, I., and KUSABAYASHI, S., 1991, *Chemistry Lett.*, 25.

[24] LUX, M., STROHRIEGL, P., and HÖCKER, H., 1987, *Makromolek. Chem.*, **188**, 811.

[25] CHAPOY, L. L., BIDDLE, D., HALSTROEM, J., KOVÁCS, K., BRUNFELDT, K., QASIM, M. A., and CHRISTENSEN, T., 1983, *Macromolecules*, **16**, 181.

[26] BILLARD, J., DUBOIS, J. C., NGUYEN HUU TINH, and ZANN, A., 1978, *Nouv. J. Chim.*, **2**, 535.

[27] KREUDER, W., and RINGSDORF, H., 1983, *Makromolek. Chem. rap. Commun.*, **4**, 807.

[28] WENDLING, J., Diploma Thesis, Darmstadt, 1992.

[29] MEIER, H., 1965, *Angew. Chem.*, **77**, 633.

[30] STOLKA, M., 1988, *Encyclopedia of Polymer Science and Technology*, Vol. 11 (John Wiley & Sons), p. 154.