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New Type of Dye Stuff for Guest-Host Liquid Crystal Displays

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New Type of Dye Stuff for Guest-Host Liquid Crystal Displays

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In this paper, we report new types of dye, tellurium bis(4-n-alkyldithiobenzoate) (TBAB), for guest-host liquid crystal displays. The electro-optical data were measured in a few mixtures of TBAB and a nematic host. The results indicate that TBAB is applicable as a guest dye for ester types of nematic host.

INTRODUCTION

Guest-host liquid crystal displays have been studied by many workers[1] since they were first described by Heilmeir, Castellano and Zanoni[2] in 1968. However, the industrial applications of guest-host displays have not been completely realized. The development of excellent dyes as the guest is one of the most important factors in removing the obstacles preventing the commercialization of guest-host displays. Most of dyes reported hitherto were limited to azo[3] and anthraquinone compounds.[4]

In the present paper, we report new types of dye for guest-host displays, tellurium bis(4-n-alkyldithiobenzoate) [R-ϕ-C(S)-S-Te-S-C(S)-ϕ-R, TBAB], which include metallic Te atom in the chromophore.

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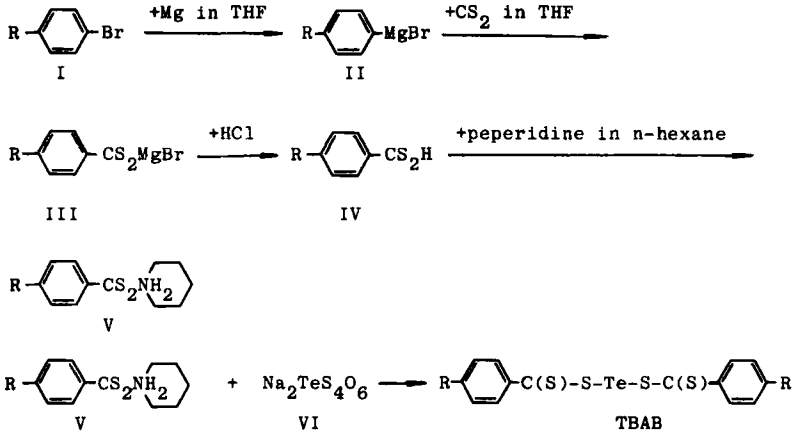
SYNTHESIS OF TBAB

TBAB was synthesized by the synthetic procedure shown in scheme 1 according to the literature.[5]



Scheme 1

Here, 4-alkylbromobenzene(I) was prepared from 4-alkylbenzenediazonium bromide and cuprous bromide,[6] and 4-alkylpiperidium dithiobenzoate(V) was snthesized through the procedure of scheme 1 according to the literature.[7] TBAB was obtained by adding 5 mmol sodium teluropentathionate(VI) in 50 ml water dropwise to 13 mmol 4-alkylpiperidium dithiobenzoate(V) in 50 ml methylene chloride. The crude sample was washed by n-hexane and recrystallized from methylene chloride solution (red needle crystals, yield: 67%). TBAB obtained was judged to be thoroughly pure by the elementary analysis and NMR. Their structures were determined by IR and NMR.

EXPERIMENTAL

The UV and visible absorptions were measured by a double beam spectrophotometer (Hitachi, 330). The anisotropic visible absorption was measured under polarized light by using a parallel orientation cell of TBAB (about 1 wt%) – host nematic solvent system. Here, the cell consists of two parallel soda glass plates (cell gap: 10 μm), which are rubbed antiparallel each other on the surface of the glass plates which were previously coated with ITO, SiO_2 and a coupling

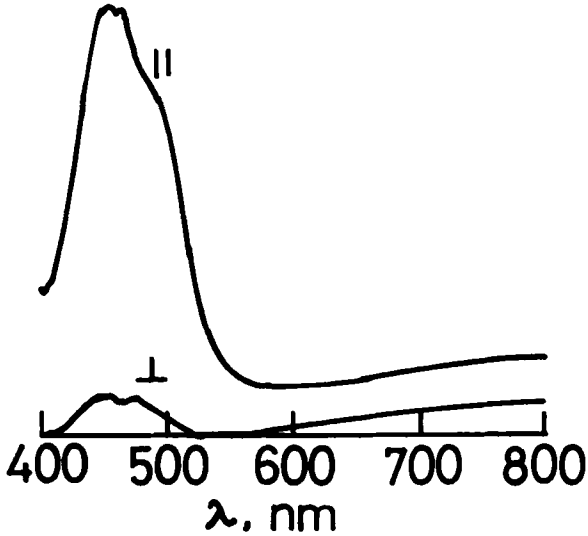


FIGURE 1 Anisotropic visible spectra for TBAB-4 (1 wt %) – EN-30 system. ∥ and ⊥: spectra in the parallel and the perpendicular direction to the director of EN-30, respectively.

agent of silane type from the substrate in turn. The melting point was measured by differential scanning calorimetry (Perkin-Elmer, DSC-IB).

RESULTS AND DISCUSSION

The physical properties of TBAB are listed in Table I. Both TBAB samples did not show a liquid crystal phase, but TBAB-5 exhibited one phase transition near 110°C in the crystalline state during heating on DSC. In both samples, no conspicuous pyrolysis was observed up

TABLE I

Physical properties of TBAB dyes

Dyes Chemical structure	Symbol	m.p. °C	UV and visible absorption[a] λ_{max} – log ε		
$(4\text{-n-}C_4H_9C_6H_4CS_2)_2Te$	TBAB-4	127.7	259-4.79	319-4.72	451-4.18
$(4\text{-n-}C_5H_{11}C_6H_4CS_2)_2Te$	TBAB-5	116.1	259-4.84	319-4.77	450-4.23

[a]The values of λ_{max} and log ε are measured in methylene chloride solution at 25°C.

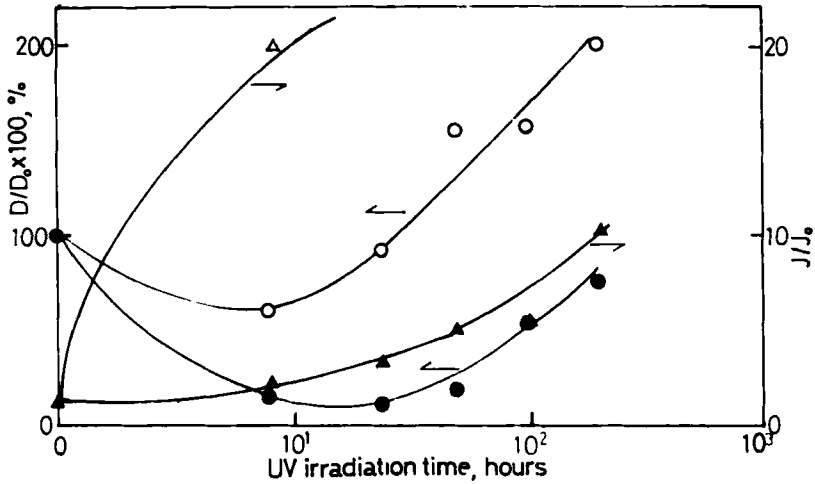


FIGURE 2 Change of optical densities and dc conductivities by UV irradiation time. ○, △: TBAB-4 – GR-61 system, ●, ▲: TBAB-4 – EN-30 system. D and D_0: optical densities at the irradiation time = 0 and t, respectively. J and J_0: dc conductivities at the irradiation time = 0 and t, respectively.

to 150°C. As shown in Table I, TBAB shows one big absorption near λ_{max} = 450 nm in visible region, by which TBAB looks yellow. The molar extinction coefficient, ϵ, is in order of 10^4 and comparable to that of anthraquinone/azo dyes. Figure 2 shows anisotropic visible spectra for TBAB-4 (1 wt%) – EN-30 (host) system. The electrooptic data are listed in Table II. Here, the values of λ_{max} and dichroic ratio, CR, are obtained for the mixtures of 1 wt% TBAB. It is noted that the values of CR and solubility are about 10 and 10%, respectively, when EN-30 is used as nematic solvent. The sum of rising and decay times was about 1.3 sec. at 20°C in the same system. Practical photochemical stability of TBAB dye was appraised by degree of fading and change of dc electrical conductivity with exposing time to UV light between 300 and 400 nm. The integral intensity of 300 to 400 nm is larger by about 42 times than the intensity of noon sunlight. The data are shown in Figure 3. Clearly the life time is more than 1000 hours under the above severe conditions. In TBAB-4 – GR-61 system, the values of J/J_0 increase rapidly with UV irradiation time, but this seems not only to be caused by TBAB dye, since a similar increase was observed in GR-61 itself. In conclusion, the above data suggest that TBAB have the adequate characteristics as a guest dye for guest-host displays, especially when the host is of the ester type.

In previous work,[1,3,4] the azo and anthraquinone dyes were shown

TABLE II

Electro-optical data for mixtures of liquid crystal host with TBAB dye

Hosts		λ_{max}		Solubility
Trade name	Main component	nm	CR	%
GR-61 (Chisso Chemical Co., Tokyo)	Cyanobiphenyl (P-Type)	465	5.0	5
EN-30 (Chisso Chemical Co., Tokyo)	Cyclohexane ester (N-Type)	455	9.6	10

to be the good guest dyes for biphenyl liquid crystal hosts. To our knowledge, good guest dyes for ester types of liquid crystal hosts have not yet been developed. In the present work, we found that TBAB dyes can be used as a guest for the ester type of liquid crystal hosts. This result attracts us towards developing various derivatives of TBAB. This work is in progress in our laboratory.

References

1. for example, T. J. Scheffer and J. Nehring, *The Physics and Chemistry of Liquid Crystal Decives*, ed. G. J. Sprokel, Plenum Press, New York (1979) p. 173.
2. G. H. Heilmeir, J. A. Castellano and L. A. Zanoni, *Mol. Cryst., Liq. Cryst.*, **8**, 293 (1969).
3. for example, J. Constant, E. P. Raynes, I. A. Shanks, D. Coates, G. W. Gray and D. C. McDonnell, *J. Phys. D.*, **11**, 479 (1978).
4. for example, M. G. Pellatt, I. H. C. Roe, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980).
5. S. Kato, Y. Itoh, Y. Ohta, K. Goto, M. Mizuta, Y. Ohno and T. Murai, *Chem. Ber.*, in press (1985).
6. T. Sandmeyer, *Ber.*, **17**, 1633 (1884).
7. S. Kato and M. Mizuta, *Bull. Chem. Soc. Japan*, **45**, 3492 (1972).