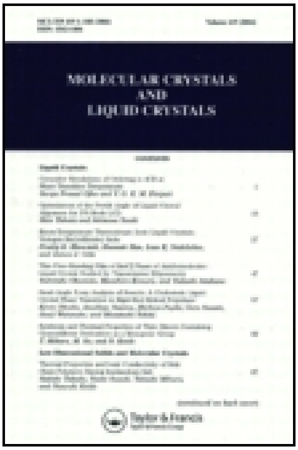


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis and some Physical Properties of 1-Cyclohexyl-2-(4″-Halobiphenyl-4′-yl)Ethanes

H. Takatsu [a] , K. Takeuchi [a] & H. Satō [a]

[a] Dainippon Ink & Chemicals, Inc., 3-35-58, Sakashita, Itabashi, Tokyo, Japan

To cite this article: H. Takatsu , K. Takeuchi & H. Satō (1983): Synthesis and some Physical Properties of 1-Cyclohexyl-2-(4″-Halobiphenyl-4′-yl)Ethanes, Molecular Crystals and Liquid Crystals, 100:3-4, 345-355

To link to this article: http://dx.doi.org/10.1080/00268948308075363

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 345–355
0026-8941/83/1004-0345/$18.50/0

Synthesis and some Physical Properties of 1-Cyclohexyl-2-(4″-Halobiphenyl-4′-yl)Ethanes

H. TAKATSU, K. TAKEUCHI and H. SATŌ

Dainippon Ink & Chemicals, Inc., 3-35-58, Sakashita, Itabashi, Tokyo, Japan

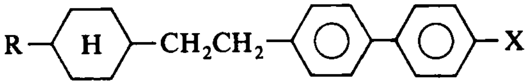
(*Received April 2, 1983*)

A series of 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes, which show nematic phases, was prepared. Their transition temperatures, enthalpies and entropies were measured. Their bulk viscosities, birefringences and dielectric constants were determined by extrapolation. 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethane has a high clearing of 125 °C, a low viscosity of 25 c.p. at 20 °C, a relatively high birefringence of 0.166 at 25 °C, and a positive dielectric anisotropy of 4.9. The transition temperatures, the N–I transition entropies, the bulk viscosities and the birefringences for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes exhibited odd-even effects in relation to the number of carbon atoms in the alkyl chain. The bulk viscosity as a function of the third power of the van der Waals radius of the halogeno group, the birefringence as a function of the van der Waals radius of the halogeno group, and the dielectric constants as a function of the dipole moment of the halogeno group are discussed for the 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes.

INTRODUCTION

Since interesting new mesomorphic compounds containing fluoro groups were reported in 1978,[1] other nematic fluoro compounds have been synthesized.[2-4] The electron attracting properties of the fluoro group can control the dielectric anisotropy and the small volume of the fluoro group does not increase the viscosity of the nematic compound. The introduction of many fluoro substituents into a nematic molecular structure gives the compound a smectic tendency[3] and the introduction of a fluoro group at the terminus of the long molecular axis decreases the clearing point compared with a typical terminal group like alkoxy or cyano.

We have synthesized a new series of 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes of formula (I) in order to achieve a nematic compound of low viscosity, weak positive dielectric anisotropy and high clearing point, and to investigate the influence of each terminal halogeno group on the transition temperature, the entropy, the bulk viscosity, the birefringence and the dielectric constants.



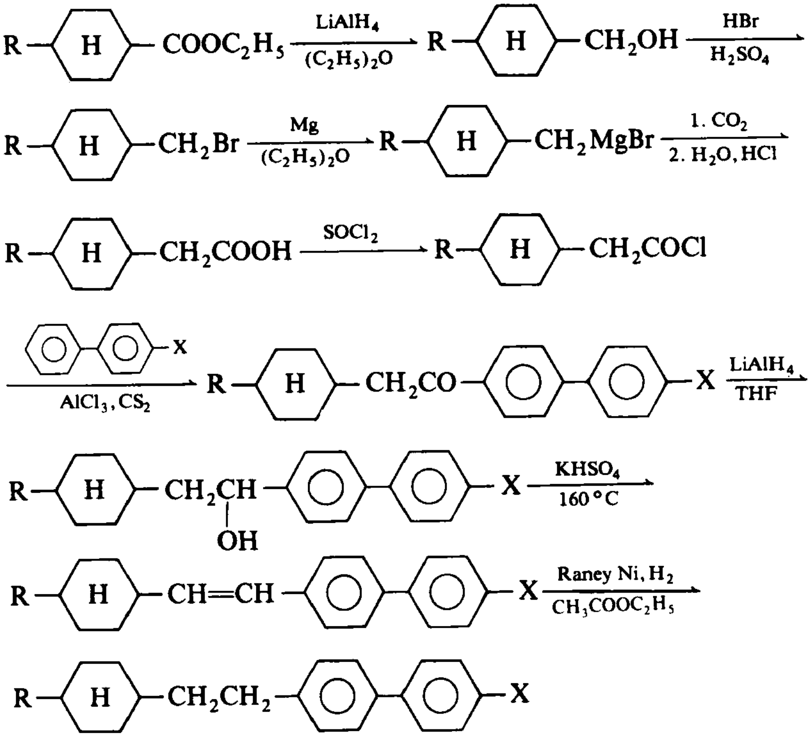
(I)

R = *n*-alkyl

X = H, F, Cl, Br

PREPARATION OF MATERIALS

The 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes were prepared according to the following scheme:



X = H, F, Cl, Br

The 4-fluorobiphenyl was prepared from phenylmagnesium bromide and *p*-iodofluorobenzene using the catalyst $PdCl_2$ in boiling THF. The 4-chlorobiphenyl and 4-bromobiphenyl were obtained commercially.

Each compound was purified by chromatography on silica gel, eluting with a mixture of hexane and benzene, followed by recrystallization from *n*-hexane/alcohol. The structures were confirmed by NMR spectrometry and mass spectrometry. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography.

RESULTS AND DISCUSSION

Mesomorphic and thermodynamic properties

The transition temperatures for the series of the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes were measured by using a polarizing microscope equipped with a heating stage. The transition enthalpies (ΔH) were measured by differential scanning calorimetry and the transition entropies (ΔS) were calculated from the enthalpies and the transition temperatures. These thermal data are listed in Table I.

The phase transition plot against alkyl chain length for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes is shown in Figure 1. The nematic-to-isotropic (N–I) temperatures exhibit the odd-even effect.

The effect of the terminal halogeno group X in formula (I) on the transition temperature can be established by comparing the transition

TABLE I

Transition temperatures, enthalpies (ΔH) and entropies (ΔS) for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes

		Transition temp. (C)		ΔH (kcal/mol)		ΔS (EU)	
R	X	C–N	N–I	C–N	N–I	C–N	N–I
C_3H_7—	H	67	82	4.04	0.254	11.9	0.715
C_3H_7—	F	76	125	3.84	0.343	11.0	0.861
C_3H_7—	Cl	100	158	4.24	0.360	11.4	0.836
C_3H_7—	Br	125	163	4.19	0.440	10.5	1.01
C_2H_5—	F	68	97	4.29	0.209	12.6	0.565
C_4H_9—	F	69	113	3.62	0.214	10.6	0.555
C_5H_{11}—	F	82	121	6.19	0.267	17.4	0.673

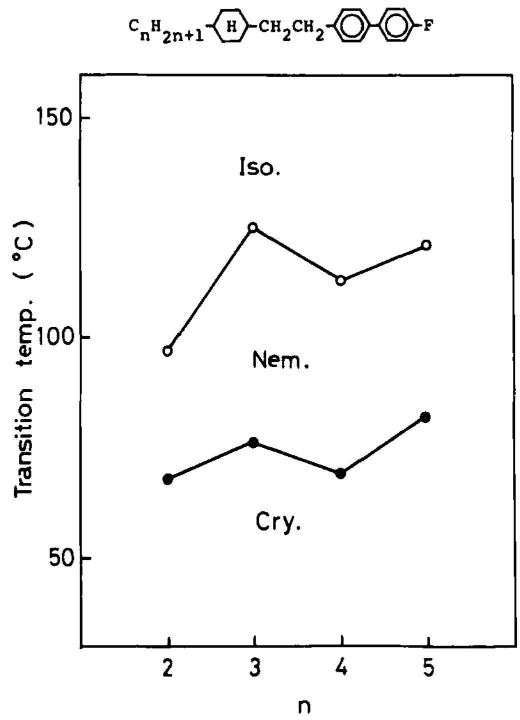


FIGURE 1 Phase transition plot against alkyl chain length (*n*) for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes: ●; Cry–Nem, ○; Nem–Iso

temperatures for the 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobophenyl-4′-yl)ethanes; R is *n*-propyl and X is H, F, Cl or Br in formula (I). With increase in the volume of the terminal halogeno group X from H → F → Cl → Br, the N–I transition temperatures increase; 43 °C from H to F, 33 °C from F to Cl, and 4 °C from Cl to Br, and the crystal-to-nematic (C–N) transition temperature also rise; 9 °C from H to F, 24 °C from F to Cl, and 25 °C from Cl to Br. The increases in the N–I transition temperatures can be explained in terms of changes in the terminal attractions. The differences in the terminal attraction for H and F and Cl are large compared with the difference for Cl and Br. The increases in the C–N transition temperature may be due to differences in the crystal structures.

The N–I and C–N transition entropies for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes are plotted against the alkyl chain length in Figure 2.

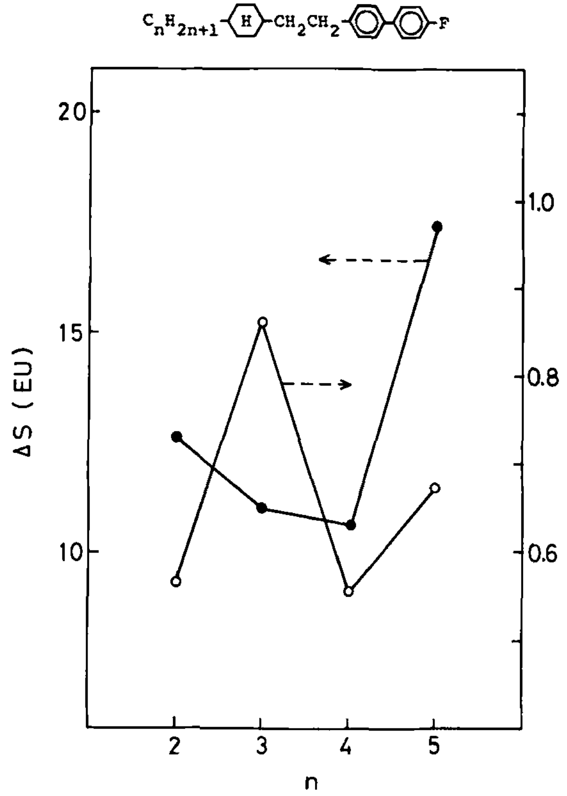


FIGURE 2 Entropy vs. alkyl chain length (*n*) for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl) ethanes: ●; Cry–Nem, ○; Nem–Iso

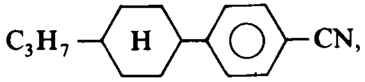
The N–I transition entropies show an odd-even effect, the odd chain lengths being associated with the higher values. Similar behaviors have been reported for 4-methylphenyl 4′-alkoxythiolbenzoates by M. Seno *et al.*[5] and for 4-, 4′-dialkoxyazoxybenzene by Arnold.[6] In these cases, the even chain lengths are associated with the higher values because of the alkoxy group. The C–N transition entropies of the homologous series from alkyl chain length 2 to 4 are almost constant, the entropy for alkyl chain length 5 then becomes larger. Similar behaviors were reported for 4-, 4′-dialkoxyazoxybenzenes by Porter *et al.*[7] The value of the C–N transition entropy of each 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethane, and of 1-(trans-4′-*n*-propylcyclohexyl)-2-(biphenyl-4′-yl)ethane remains nearly constant, being in the range 10.5–11.9 EU.

Physical properties

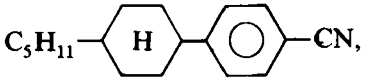
As the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes do not exhibit nematic phases at room temperature, their bulk viscosities at 20 °C, birefringences at 25 °C, and dielectric constants at 25 °C were determined by extrapolation from data obtained using a series of solutions of the compounds in a mixture of substituted phenyl cyclohexanecarboxylates[8] and 4-substituted 1-(4′-cyanophenyl)cyclohexanes[9]; results are listed in Table II. The composition and physical properties of the mixture used as host are as follows:

composition:

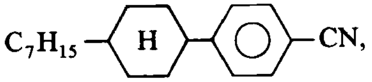
20 wt% of



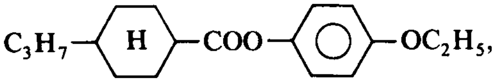
16 wt% of



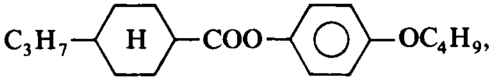
16 wt% of



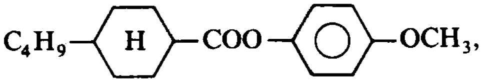
8 wt% of



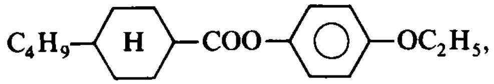
8 wt% of



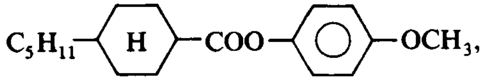
8 wt% of



8 wt% of

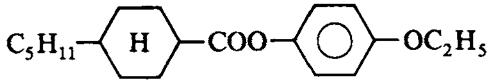


8 wt% of



and

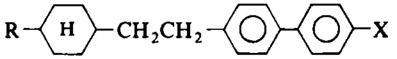
8 wt% of



N–I transition temperature: 54.0 °C
bulk viscosity at 20 °C: 21.0 c.p.
birefringence at 25 °C: 0.0917
dielectric anisotropy at 25 °C: 6.6

TABLE II

Bulk viscosities at 20 °C, birefringences at 25 °C, and dielectric constants at 25 °C of the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes



R	X	Bulk viscosity at 20 °C (c.p.)	Birefringence at 25 °C (—)	Dielectric constants (—)		
				$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
C_3H_7—	H	22.7	0.148	3.50	1.38	2.12
C_3H_7—	F	25.1	0.166	6.32	1.43	4.89
C_3H_7—	Cl	46.6	0.220	8.83	1.33	7.50
C_3H_7—	Br	63.0	0.234	8.51	1.36	7.15
C_2H_5—	F	24.8	0.140	6.51	1.95	4.56
C_4H_9—	F	36.0	0.155	5.71	1.18	4.53
C_5H_{11}—	F	31.3	0.165	5.56	1.29	4.27

The viscosity measurements were made using a rotating coneplate viscometer at 20 °C. The bulk viscosities for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes are plotted against the alkyl chain length in Figure 3. The bulk viscosities increase with increase in the alkyl chain length, showing the trend of an odd-even effect. The bulk viscosity of 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethane is 25.1 c.p. at 20 °C, which is extremely low compared with the viscosities of other nematic compounds having high clearing points over 100 °C. The bulk viscosities for the 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes increase with increase in the volume of the terminal group from H → F → Cl → Br. The bulk viscosity as a function of (van der Waals radius of halogeno group)^3 is shown in Figure 4. A linear relationship between the logarithm of the bulk viscosity and (van der Waals radius of halogeno group)^3 is obtained. The logarithm of the bulk viscosity increases linearly with increase in the volume of the terminal group. This result is referred to in the following equations:[10]

$$\eta \alpha \exp(\Delta G/RT) \qquad \Delta G = P\Delta V + \Delta U$$

where, η : viscosity
G : free energy
R : gas constant
T : absolute temperature
P : pressure
V : volume
U : internal energy

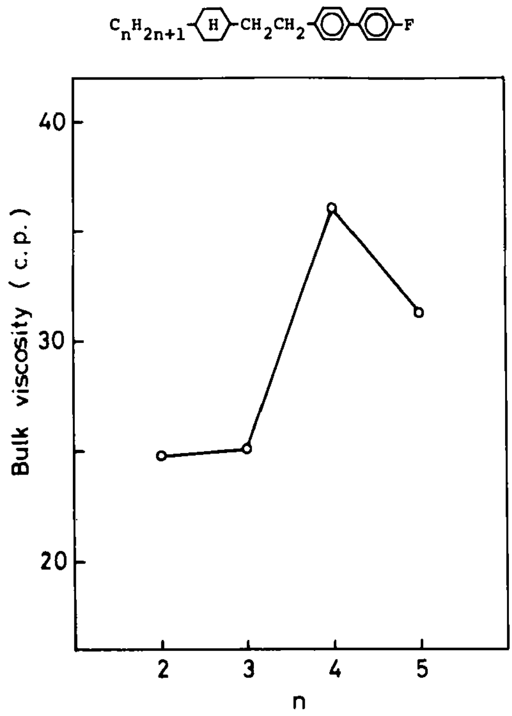


FIGURE 3 Bulk viscosity vs. alkyl chain length (*n*) for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes

Birefringences were measured by polarizing microscopy using a compensator. The birefringences for the 1-(trans-4′-*n*-alkylcyclohexyl)-2-(4″-fluorobiphenyl-4′-yl)ethanes are plotted against the alkyl chain length in Figure 5. The birefringences exhibit an odd-even effect, odd chain lengths being associated with higher values as for the N–I transition temperatures and the N–I transition entropies. A similar odd-even effect of birefringence was reported for 4-methyl-4′-alkylazobenzenes and 4-ethyl-4′-alkylazobenzenes by Dabrowski *et al.*[11] This shows that differences in molecular conformation between odd and even members influences the birefringence. The birefringences increase as the halogeno groups become larger, and a terminal halogeno group conjugated with an aromatic system apparently enhances the birefringence. The birefringences for the 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes are plotted as a function of van der Waals radius of the terminal group in Figure 6. This shows a linear relationship between the birefringence and the van der

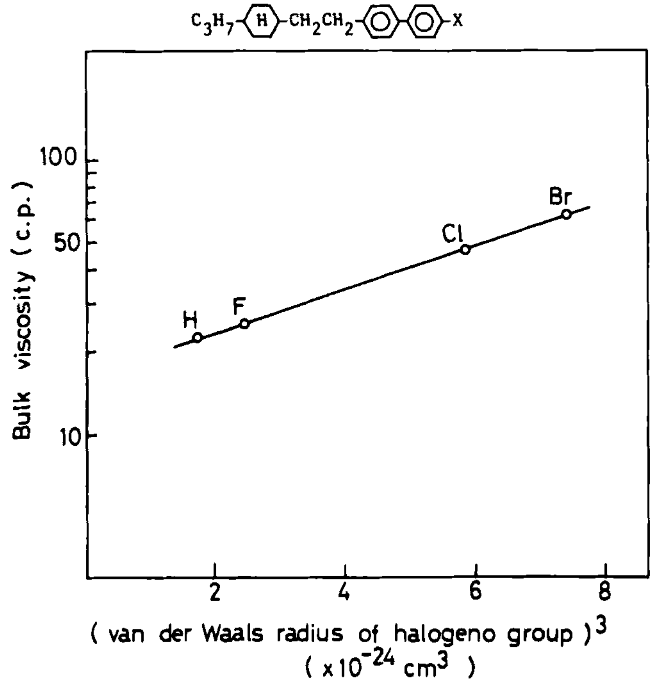


FIGURE 4 Bulk viscosity vs. (van der Waals radius of the terminal group)^3 for the 1-(trans-4'-*n*-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl) ethanes

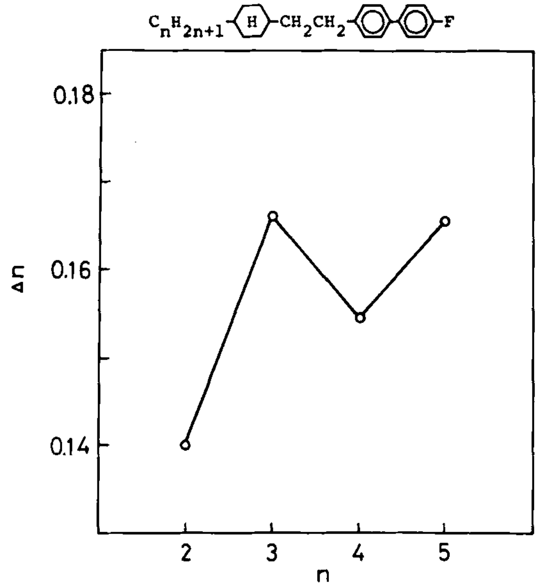


FIGURE 5 Birefringence (Δn) vs. alkyl chain length (n) for the 1-(trans-4'-*n*-alkylcyclohexyl)-2-(4''-fluorobiphenyl-4'-yl)ethanes

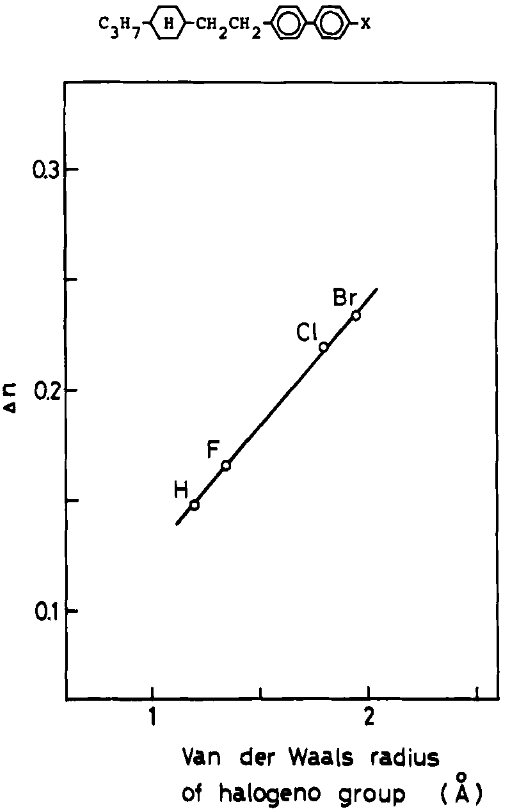


FIGURE 6 Birefringence (Δn) vs. van der Waals radius of the terminal group for the 1-(trans-4′-*n*-propylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes

Waals radius of the terminal group, such that the birefringence increases linearly with increase in the ratio of the length of the conjugated part of the molecule to the total molecular length.

The dielectric constants were determined from the capacitance of a parallel-plate capacitor measured empty and then filled with liquid crystal. The dipole moment of the terminal halogeno group enhances the dielectric constant parallel to the optical axis ($\epsilon_{\parallel}$) and as a result enhances the dielectric anisotropy ($\Delta\epsilon$). The dielectric constants ($\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\Delta\epsilon$) are related linearly to the dipole moment of the terminal halogeno group as shown in Figure 7.

Acknowledgement

The authors would like ot thank Miss T. Kanō for the determinations of the transition enthalpies and entropies.

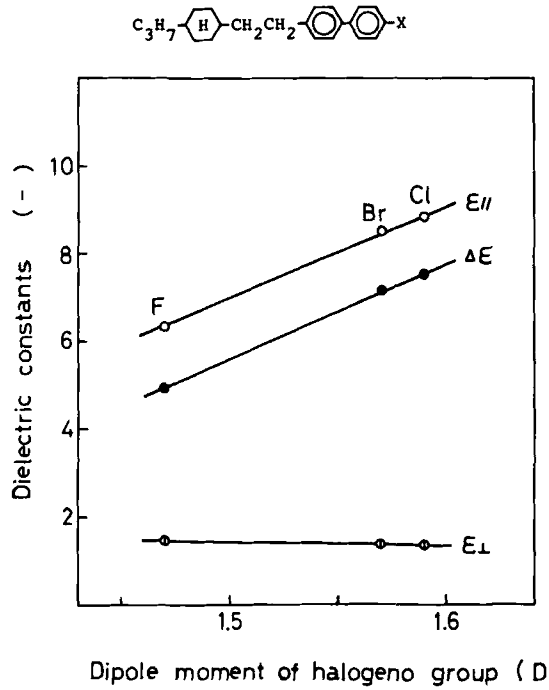


FIGURE 7 Dielectric constant vs. dipole moment of the halogeno group for the 1-(trans-4'-*n*-propylcyclohexyl)-2-(4"-halobiphenyl-4'-yl)ethanes

References

1. A. Béguin and J. C. Dubois, *7th Inter. Liq. Cryst. Conf.*, AP-1 (1978).
2. G. W. Gray, C. Hogg, and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **67**, 1 (1981).
3. A. V. Ivashchenko, E. I. Kovshev, V. T. Lazareva, E. K. Prudnikova, V. V. Titov, L. M. Yagupdsky, T. I. Zverkova, and M. I. Barnik, *8th Inter. Liq. Cryst. Conf.*, E-22P (1980).
4. S. Sugimori, *7th Ekishō Tōronkai*, 4V-02 (1981).
5. Y. B. Kim and M. Seno, *Mol. Cryst. Liq. Cryst.*, **36**, 293 (1976).
6. H. Arnold, *Mol. Cryst. Liq. Cryst.*, **2**, 63 (1966).
7. R. S. Porter, E. M. Barrall II, and J. F. Johnson, *Accounts Chem. Res.*, **2**, 53 (1969).
8. D. Demus, H. -J. Deutcher, F. Kuschel, and H. Schubert, DOS No. 24 29 093 (1975).
9. R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, *Angew. Chem. Intern. Ed.*, **16**, 100 (1977).
10. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
11. R. Dabrowski, K. Kenig, Z. Raszewski, and J. Kedzierski, *Mol. Cryst. Liq. Cryst.*, **61**, 61 (1980).