Syntheses and Thermal Properties of New Liquid Crystalline Materials Involving Tropolone

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SUMMARY

To examine the effect of a tropolone ring system on mesomorphic behavior, the following 2- and 3-ring compounds have been prepared. The 2-ring

$$R = C_n H_{2n+1}, \quad C_n H_{2n+1}O \qquad Y = OH, \; OCH_3$$
$$X = -CH=N-, \quad -N=N-$$
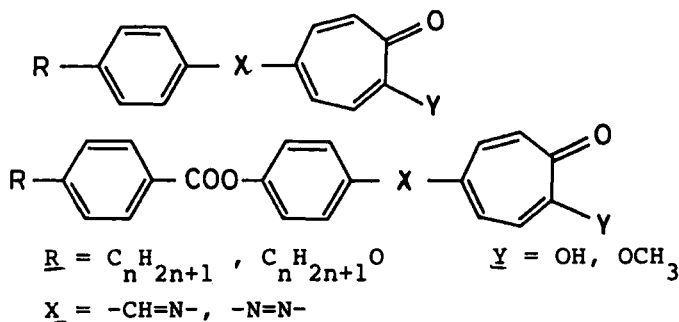
compounds are non-mesogenic whereas the 3-ring compounds exhibit nematic phases of high stability when R = alkyl or alkoxy, $X = -CH=N-$

or —N=N—, and Y = OH or OCH_3, and an additional smectic phase when R = alkoxy. The nematic phase tends to align homeotropically when placed between two glass plates.

INTRODUCTION

An investigation of the physical properties of new liquid crystalline materials is important in studying a relationship between the structure of materials and their mesomorphic characteristics. Liquid crystalline materials having a polar group such as cyano or nitro give rise to some interesting behaviors and some of these have successfully proved useful in electro-optical devices employing the twisted nematic mode.
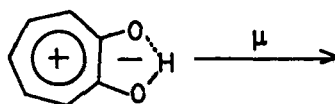
Tropolone is a seven membered ring compound with a carbonyl and a hydroxy group. The polar structure shown below forms a 6π electron system and stabilizes the conjugated system.[1] Thereby, the polar structure induces a powerful dipole moment along the major molecular axis, as shown below. The dipole moment of tropolone (3.5 D)[2] is comparable with

that of benzonitrile (3.9 D).[3] Hence, tropolone will be suitable as a terminal group for high stability of liquid crystalline materials. In this paper, we will report the syntheses and thermal properties of some new liquid crystalline materials containing the tropolone ring system.

Compound	R	X	Y
I	alkoxy	—CH=N—	OH
II	alkoxy	—N=N—	OH
III	alkoxy	—N=N—	OCH_3
IV	alkyl	—CH=N—	OH
V	alkoxy	—CH=N—	OH
VI	alkoxy	—N=N—	OH
VII	alkoxy	—N=N—	OCH_3

EXPERIMENTAL

Melting points and transition temperatures were determined using a Nikon POH polarizing microscope equipped with a Mettler FP 52 heating stage

and FP 5 control unit. Transition enthalpies were determined using a Daini-Seikosha model SSC–560 differential scanning calorimeter. Indium (99.9%) was used as a calibration standard with a heating rate of 5°C/min. Dielectric constants were measured using a General Radio 1621 precession capacitance-measurement system. The capacitor cell consisted of two tin oxide coated glass electrodes separated by 12μ Mylar spacer. The cell temperature was controlled by a brass housing. The voltage applied was 0.1 volt at 1 KHz. An alignment of molecules was achieved by rubbing. The virtual nematic isotropic transition temperatures[4] for series I, II, and III were estimated by extrapolation for the binary phase diagrams of the systems of these compounds and 3-(4'-ethoxybenzylidene)amino-N-methylcarbazole (T_{NI} = 164.0°C; ΔH_{NI} = 0.71 KJmole^{-1}, T_{CN} = 144.0°C; ΔH_{CN} = 13.38 KJmole^{-1}).[5] The accuracy is assumed to be ±5°C.

MATERIALS

5-Aminotropolone   To a solution of tropolone (0.10 mole) in water (35 ml) was added sodium nitrite (0.11 mole) in acetic acid (30 ml) at 5°C. After stirring for 3 hrs at room temperature, the solid precipitated was collected by filtration, giving 5-nitrosotropolone as a yellow powder (13.1 g, 87%). *5-Nitrosotropolone* (0.06 mole) was hydrogenated in ethanol (100 ml) at ~50 in^2 in the presence of platinum oxide (30 mg). After removal of the catalyst, the solvent was distilled off. The residue was purified by sublimation, followed by recrystallization from ethyl acetate, giving 5-aminotropolone as yellow needles (6.2 g, 75%), mp. 177–178°C.[6]

5-(4'-Propoxybenzylidene)aminotropolone   A solution of 5-aminotrop-olone (0.015 mole) and 4-propoxybenzaldehyde (0.015 mole) in absolute ethanol (12 ml) was refluxed for 2 hrs.[7] The precipitate obtained was re-crystallized from absolute ethanol, giving 5-(4'-propoxybenzylidene) aminotropolone as yellow needles (3.40 g, 80%).

5-(4'-Propoxyphenyl)azotropolone   To a solution of 4-propoxyphenyl dia-zonium sulfate which was prepared by the reaction of 4-propoxyaniline (0.012 mole) with sodium nitrite was added tropolone sodium salt (0.01 mole) at 0°C, and the resulting solution left at room temperature overnight.[8] The solution was extracted with chloroform. After removal of the solvent, the product was purified by column chromatography on silica gel, using

chloroform as the eluting solvent, and then recrystallized from ethanol, giving 5-(4'-propoxyphenyl)azotropolone as orange needles (1.70 g, 60%).

5-(4'-Propoxyphenyl)azo-2-methoxytropone   To a solution of 5-(4'-propoxyphenyl)azotropolone (0.004 mole) in methanol (7 ml) was added the ethereal solution of diazomethane until the ferric trichloride test became negative.[9] After removal of solvent, the residue was purified by column chromatography on silica gel using chloroform as the eluting solvent, and then recrystallized from ethanol, giving 5-(4'-propoxyphenyl)azo-2-methoxytropone as orange needles (0.87 g, 73%).

Compounds IV, V, VI, and VII were prepared similarly.

Purity of the materials was checked by elementary analysis and thin layer chromatography on silica gel. The elementary analysis data are shown below.

Compound	n	Formula	Calculated (%)			Found (%)		
			C	H	N	C	H	N
I	3	$C_{17}H_{17}NO_3$	72.07	6.05	4.94	71.98	6.18	4.79
	6	$C_{20}H_{23}NO_3$	73.82	7.12	4.30	73.67	7.10	4.25
II	3	$C_{16}H_{16}N_2O_3$	67.59	5.67	9.85	67.51	5.72	9.68
	6	$C_{19}H_{22}N_2O_3$	69.92	6.79	8.58	69.77	6.85	8.34
III	3	$C_{17}H_{18}N_2O_3$	68.44	6.08	9.39	68.35	6.01	9.11
	6	$C_{20}H_{24}N_2O_3$	70.57	7.11	8.23	70.52	7.16	8.06
IV	0	$C_{21}H_{15}NO_4$	73.04	4.38	4.06	72.95	4.35	3.88
	1	$C_{22}H_{17}NO_4$	73.53	4.77	3.90	73.38	4.77	3.74
	2	$C_{23}H_{19}NO_4$	73.98	5.13	3.75	73.88	5.21	3.57
	3	$C_{24}H_{21}NO_4$	74.40	5.46	3.62	74.31	5.41	3.44
	4	$C_{25}H_{23}NO_4$	74.80	5.77	3.49	74.71	5.86	3.33
	5	$C_{26}H_{25}NO_4$	75.16	6.07	3.37	74.84	6.00	3.10
	6	$C_{27}H_{27}NO_4$	75.50	6.34	3.26	75.33	6.38	3.08
	7	$C_{28}H_{29}NO_4$	75.82	6.59	3.16	75.74	6.43	3.01
	8	$C_{29}H_{31}NO_4$	76.12	6.83	3.06	75.91	6.78	2.94
V	1	$C_{22}H_{17}NO_5$	70.39	4.56	3.73	70.22	4.63	3.69
	2	$C_{23}H_{19}NO_5$	70.94	4.92	3.60	70.79	4.88	3.47
	3	$C_{24}H_{21}NO_5$	71.45	5.25	3.47	71.37	5.29	3.24
	4	$C_{25}H_{23}NO_5$	71.93	5.55	3.36	71.69	5.47	3.21
	5	$C_{26}H_{25}NO_5$	72.37	5.84	3.25	72.16	5.94	3.05
	6	$C_{27}H_{27}NO_5$	72.79	6.11	3.14	72.67	6.00	3.02
	7	$C_{28}H_{29}NO_5$	73.18	6.36	3.05	72.91	6.25	2.89
	8	$C_{29}H_{31}NO_5$	73.55	6.60	2.96	73.37	6.49	2.67
VI	3	$C_{23}H_{20}N_2O_5$	68.31	4.98	6.93	68.21	4.87	6.76
	4	$C_{24}H_{22}N_2O_5$	68.89	5.30	6.69	68.78	5.18	6.53
	5	$C_{25}H_{24}N_2O_5$	69.43	5.59	6.48	69.27	5.47	6.31
	6	$C_{26}H_{26}N_2O_5$	69.94	5.87	6.27	69.86	5.94	6.01
	7	$C_{27}H_{28}N_2O_5$	70.42	6.13	6.08	70.36	6.09	5.94
VII	3	$C_{24}H_{22}N_2O_5$	68.89	5.30	6.69	68.74	5.22	6.67
	4	$C_{25}H_{24}N_2O_5$	69.43	5.59	6.48	69.17	5.48	6.24
	5	$C_{26}H_{26}N_2O_5$	69.94	5.87	6.27	69.73	5.81	6.05
	6	$C_{27}H_{28}N_2O_5$	70.42	6.13	6.08	70.18	6.20	5.84
	7	$C_{28}H_{30}N_2O_5$	70.87	6.37	5.90	70.71	6.45	5.68

RESULTS AND DISCUSSION

Thermal properties

Transition temperatures for two ring compounds I, II, and III are summarized in Table I. The members of series I and II have appreciably high melting points and do not exhibit mesomorphic properties under the usual conditions: the virtual nematic-isotropic transition temperatures ranging from 42 to 47°C. These values are considerably lower than those of 4-(4'-alkoxybenzylidene)aminobenzoic acids (T_{NI} = 240 − 270°C).[10] Considering the fact that the hydrogen bonded dimer of the acids is the origin of formation of the liquid crystallinity,[11] the lower values indicate that series I and II in which the hydroxy proton is slightly acidic (pKa = 6.92)[12] do not form the hydrogen bonded dimer.

The methyl ethers III also exhibit high melting points and do not form any mesophase. The virtual nematic-isotropic transition temperatures are similar to those for series II.

Table II indicates the thermal properties of series IV and V. The members of the former form only a nematic phase, while the latter forms the nematic and smectic ones which commences at the butoxy homologue. In both series the nematic phase tends to align homeotropically when placed in between two glass plates, presumably due to strong interactions between the terminal hydroxy and carbonyl groups and the glass surface. The smectic phase shows a typical fan shaped texture. The tropolone skeleton tends to decompose above 240°C. In Figure 1 are plotted the nematic-isotropic transition temperatures against the carbon number n. In series IV, the transition temperatures show an apparent even odd effect, though the transition enthalpies and entropies show no regular trend. The transition temperatures for series IV also show the similar trend with a little alternation.

TABLE I

Transition temperatures (°C) of I, II, and III

Compound	n	C		I	T_{NI} (virtual[1])
I	3	·	139.2	·	44
	6	·	151.8	·	42
II	3	·	177.2	·	49
	6	·	151.2	·	42
III	3	·	161.2	·	50
	6	·	152.2	·	53

[1]Refer to the experimental section.

S. TAKENAKA, S. KUSABAYASHI and S. SETO

TABLE II

Transition temperatures (°C) and enthalpies of IV and V

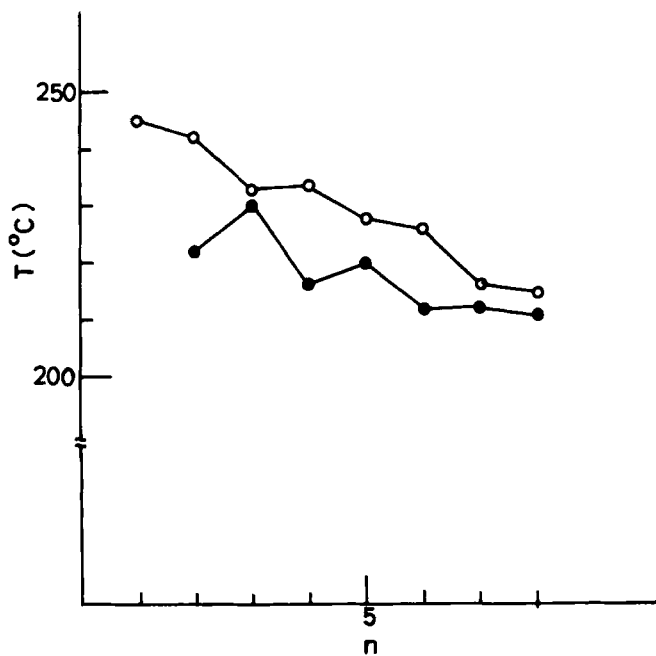| Compound	n	C		S	N		I	ΔH (KJ mol^{-1})
IV	0	•	198.5	–	–		•	
	1	•	197.1	–	•	230.2[1]	•	
	2	•	199.4	–	•	222.3	•	1.7
	3	•	200.1	–	•	230.6	•	1.5
	4	•	185.5	–	•	216.3	•	1.8
	5	•	176.5	–	•	219.6	•	2.7
	6	•	173.5	–	•	212.2	•	1.7
	7	•	176.0	–	•	202.1	•	2.4
	8	•	174.5	–	•	201.1	•	2.5
V	1	•	220.2	–	•	244.8[2]	•	
	2	•	218.4	–	•	242.1[2]	•	
	3	•	174.8	–	•	233.5	•	3.5
	4	•	143.8	• 166.3	•	233.7	•	7.9
	5	•	129.0	• 163.5	•	227.5	•	5.1
	6	•	125.9	• 162.0	•	225.8	•	6.2
	7	•	108.8	• 161.0	•	215.8	•	5.2
	8	•	138.2	• 164.5	•	214.1	•	5.5

[1]This decomposed above 230°C. [2]These decomposed above 240°C.

FIGURE 1   Plots of nematic-isotropic transition temperatures against the number (n) of the carbon atoms in the alkyl or the alkoxy chain for series IV (●) and V (○).

Table III indicates the thermal properties of series VI and VII. In VI the smectic phase with a fan shaped texture commences at the hexyloxy homologue. The methylation of the hydroxy group in VI tends to lower the stability of the smectic phase. The averaged nematic-isotropic transition temperatures and the enthalpies and entropies for the pentyl to heptyl homologues or the pentyloxy to heptyloxy homologues are summarized below.

	IV	V	VI	VII
$T(°C)$	211.3	223.0	228.8	201.4
$\Delta H(KJmole^{-1})$	2.27	5.50	1.53	0.60
$\Delta S(JK^{-1}mole^{-1})$	4.69	11.1	3.05	1.26

The transition temperatures decrease by the order of series VI > V > IV > VII. On the other hand, the effective order for the transition enthalpies or the entropies is series V > IV > VI > VII, which is analogous to that for the dielectric anisotropy which will be shown in the later section, indicating that the dipolarity of the molecules is a dominative factor in determining the thermal properties of the nematic phase.

That is, the powerful dipole moment (3.5 D) along the longer molecular axis, as shown in (A) in Figure 2, would be expected to increase the polarity and polarizability of the molecules, a general requisite for enhancing the thermal stability of a mesophase. Indeed, the averaged value (228.8°C) for series VI is higher by ca. 85°C than the averaged transition temperatures for the pentyloxy to heptyloxy homologues of 4-(4'-alkoxybenzoyloxy)phenylazobenzenes.[13]

TABLE III

Transition temperatures (°C) and entropies of VI and VII

Compound	n	C		S		N		I	ΔH (KJ mol^{-1})
VI	3	•	194.0	–		•	240.5[1]	•	
	4	•	181.9	–		•	240.8[1]	•	
	5	•	184.6	–		•	234.8	•	1.4
	6	•	179.0	•	186.1	•	232.0	•	1.5
	7	•	152.8	•	184.8	•	219.7	•	1.7
VII	3	•	168.7	–		•	223.5[2]	•	
	4	•	167.0	–		•	218.4[2]	•	
	5	•	173.3	–		•	204.3	•	0.3
	6	•	173.3	–		•	203.4	•	0.8
	7	•	171.8	–		•	196.6	•	0.7

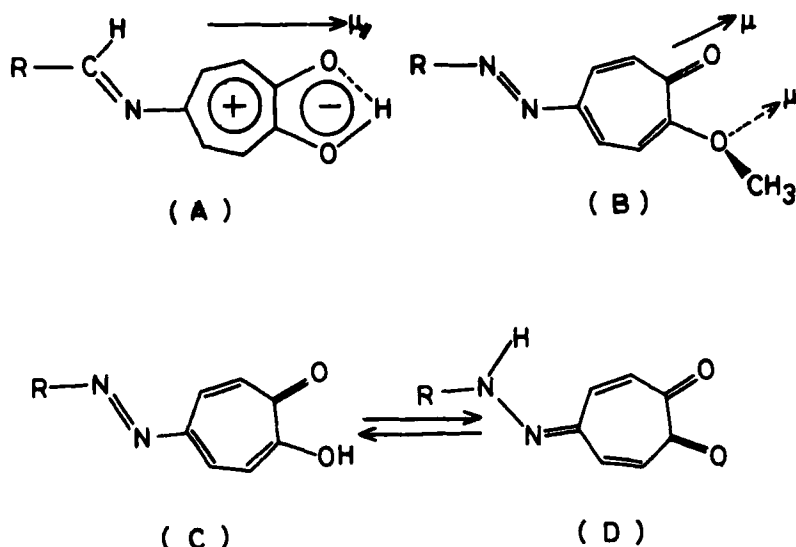[1]These compounds decomposed above 240°C. [2]These compounds decomposed above 220°C.

FIGURE 2   Variations of dipole moments around the seven membered ring.

An interesting fact in the homologous series is that the transition enthalpies and also entropies rather than the transition temperatures are influenced by the electronic natures of the tropolone ring. This suggests that the order parameter within the nematic phase and therefore the transition entropy on passing from the nematic phase to the isotropic solution is strongly influenced by the dipolarity and polarizability of the molecules.

In fact, the effective order for the transition enthalpies or the entropies is well correlated with the electronic natures of the molecules. The difference in the transition enthalpies for series IV and V, and also the transition temperatures should be attributed to the greater polarity of the terminal ring in V, due to mutual conjugation between the alkoxy and azomethine groups. The transition enthalpies for series IV and V are larger than those for series VI and VII. The following fact is worthy of note. In 5-azotropolone compounds the tautomerization shown in Figure 2 has been known to occur,[14] where the keto form (D) is unfavorable for the mesophase stability since the increased single bond character of the — N == N — bond in (D) will lead to an increase in conformational flexibility and a decrease in mutual conjugation along the entire molecule.

As is evident from the comparison between series II and III, or series VI and VII, the methylation of the hydroxy group does not enhance the nematic stability, rather decreases it, whereas it elongates the molecular

length. A possible explanation is that the methylation decreases the dipolarity arising from the polar structure (A), and results in dispersion of the dipolarity, as shown in (B) in Figure 2, decreasing the anisotropies of polarity and polarizability. Moreover, the methylation will lead to increase the molecular breadth, since the methyl group in III and VII has been known to locate on the seven membered ring due to steric interaction between the methoxy and the adjacent carbonyl groups.[15] The increased molecular breadth would weaken the interaction forces, resulting in decrease in the transition temperatures and also the enthalpies.

Another fact being worthy of note for the characteristics of tropolone is that tropolone (6.4 Å)[16] has larger molecular breadth compared with that of benzene (4.8 Å). The increased molecular breadth will weaken the interaction forces, decreasing the stability of the mesophase. Indeed, the averaged value (219°C) of the transition temperatures for the hexyloxy to octyloxy homologues of series V is lower by 45°C than that for the hexyloxy to octyloxy homologues of 4-cyano-(4'-(4''-alkoxybenzoyloxy)-benzylidene)anilines,[17] presumably due to the increased molecular breadth around the seven membered ring. Thus, the trends of the transition temperatures and the enthalpies are well correlated with the characteristics of tropolone.

DIELECTRIC PROPERTIES

The dielectric constants were taken in a eutectic mixture of 4-ethylphenyl-4'-methoxyazoxybenzene, where the nematic range was from −5 to 73°C, since the tropolone compounds prepared here had relatively high melting points. The dielectric constant of the eutectic mixture is 5.20 for $\varepsilon_\parallel$ and 5.41 for $\varepsilon_\perp$, and the anisotropy $\Delta\varepsilon$ is −0.21.[18] The results are shown in Figure 3. The dielectric constants for both parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) directions tend to increase linearly with increasing the composition of the tropolone compounds. For the propoxy homologue $\varepsilon_\parallel$ of I is slightly larger than $\varepsilon_\perp$, giving rise to the large positive value of $\Delta\varepsilon$. The dipole moment directing to the longer molecular axis [depicted by arrow in structure (A)] is assumed to be responsible for the large $\Delta\varepsilon$. For the butoxy homologue of VII, on the other hand, both $\varepsilon_\parallel$ and $\varepsilon_\perp$ are comparatively large, though the difference is not so large. In this case, the dipole moments originated from the carbonyl group and the ether oxygen of tropone will make some angles to the long axis of the molecule, as shown in (B) in Figure 2, consequently resulting in increase in both dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$.

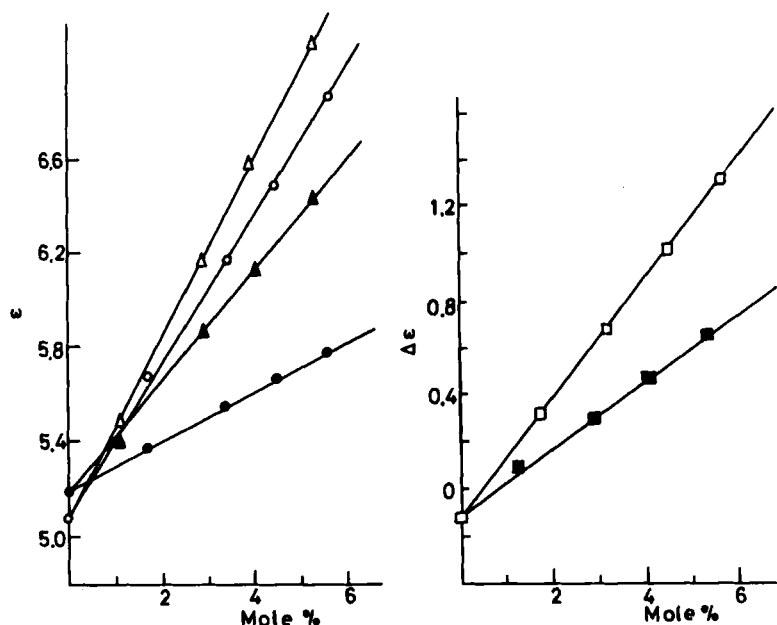S. TAKENAKA, S. KUSABAYASHI and S. SETO

FIGURE 3   (a) Dielectric constants for parallel (O) and perpendicular directions (●) for the propoxy homologue of I, and parallel (△) and perpendicular directions (▲) for the butoxy homologue of VII. (b) Dielectric anisotropies for the proxy homologue of I (□) and the butoxy homologue of VII (■).

Supposing that the lines in Figure 3 are proportional to the composition of the tropolone compounds over the whole range, the anisotropies of the dielectric constants for the neat solution are extrapolated as follows. All tropolone compounds have large positive dielectric anisotropies. The values of $\Delta\varepsilon$ are comparable with those for 4-(4′-alkoxybenzylidene)aminobenzo-nitriles ($\Delta\varepsilon = \sim20$).[19] The dipolarity of tropolone should be responsible for the large $\Delta\varepsilon$. The effective order for $\Delta\varepsilon$, V > VI > I > VII > II is similar to that for the enthalpy change, and therefore should be explicable in terms of change in dipolarity around the tropolone ring. A remarkable trend in the related series is that $\Delta\varepsilon$ of the azomethine compounds are always larger than those of azo derivatives, i.e., I > II, and V > VI. The dielectric constants for both $\varepsilon_\parallel$ (47.2) and $\varepsilon_\perp$ (18.2) of the propoxy homo-logue of V are slightly larger than those ($\varepsilon_\parallel = 29.3$, and $\varepsilon_\perp = 4.88$) for the butoxy homologue of VI, presumably due to the fact that the tautomer (D) in Figure 1 weakens the conjugative interactions between the aromatic rings, decreasing the dipolarity.

For VII the disappearance of the polar structure (A) by the methylation of the hydroxy group might be the cause of the lower $\Delta\varepsilon$.

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