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Ultraviolet stability of liquid crystals containing cyano and isothiocyanato terminal groups

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The ultraviolet (UV) stabilities of liquid crystal compounds containing cyano (CN) and isothiocyanato (NCS) terminal groups are compared. UV exposure is found to degrade the clearing temperature, birefringence, dielectric constants and visco-elastic coefficient of the liquid crystal compounds. The measured data show that the NCS molecular structure exhibits a better UV stability than do the corresponding CN structures. Lewis resonance structures are used to explain this phenomenon.

1. Introduction

Liquid crystals (LCs) are used extensively for direct-view displays, projection displays and photonic devices [1–3]. Material stability is a primary concern for all devices desired to have a long operational lifetime [4]. In direct-view displays, ultraviolet (UV) light is often used to seal the LC panel. In projection displays, the employed arc lamp is extremely bright; although a cold mirror and a hot mirror are used to filter out the unwanted UV and infrared contents of the lamp, residual UV light could still reach the LC panel and cause a gradual degradation of the LC molecules. Once the LC medium is damaged, the pretilt angle is changed so that the consequent electro-optic effects are altered. Therefore, it is critical to identify the ultimate LC material failure mechanism and search for molecular structures that can withstand a longer UV exposure.

The most common nematic LC structure for displays consists of an alkyl chain, one or two cyclohexane rings, a phenyl ring, and a polar group. The saturated σ-bonds in the alkyl chain and cyclohexane ring are very stable because their absorptions occur in the deep UV region ($\lambda \sim 120\,\mathrm{nm}$) which is far from the commonly used UV line $\lambda = 365\,\mathrm{nm}$. For active matrix LCD applications, fluoro (F) is the preferred polar group as it exhibits a high resistivity, low viscosity and low birefringence [5, 6]. However, both cyano (CN) [7] and isothiocyanate (NCS) [8] are the popular choices for use in most passive matrix LCD, because they exhibit a large dipole and contribute to the enhancement of the birefringence. In a CN group, the carbon and nitrogen atoms are linked by a triple bond, whereas in NCS there are two double bonds. The conjugation length calculated from the carbon on the phenyl ring to the terminal CN or NCS group is 2.585 and 3.887 Å, respectively. The calculations were based on the HyperChem V7.0 simulation software with Austin Modal 1 (AM1). Due to its more elongated structure, NCS makes a larger contribution to birefringence than CN. Moreover, an NCS compound exhibits a much lower viscosity than a CN compound because it's molecules do not form dimers. However, the CN group has a larger dipole moment than NCS. Thus, both CN and NCS have been widely used as terminal groups for display and photonic applications.

To compare the UV stability of the CN and NCS groups, we carefully chose three similar LC structures, PP-5CN (commonly known as 5CB), CP-5CN (5PCH) and CP-6NCS (6CHBT), for studies. Here, P stands for the phenyl ring and C for the cyclohexane ring. The molecular structure, phase transition temperatures, and birefringence of these three compounds are listed in the table. They are all two-ring structures with an alkyl side chain and a polar group, and have been used extensively in the display industry. All three compounds have a nematic phase at room temperature; this feature is particularly attractive because we can measure their physical properties at room temperature without making guest–host mixtures and then using extrapolated results.

2. Experimental

The LC molecules under study are relatively stable; therefore, the necessary UV exposure was expected to be lengthy. The exposure took place at room temperature

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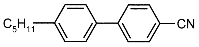
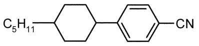
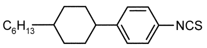
Table. Structure, phase transition temperatures (in °C) and birefringence (Δn at $T=23°C$ and $\lambda=633$ nm) of the three LC compounds studied. Cr, N and I represent crystalline, nematic and isotropic phase, respectively. Due to supercooling, 5CB remains in the nematic phase at room temperature.

Compounds	Molecular structure	Phase transitions	Δn
5CB(PP5CN)		Cr 24 N 35.3 I	0.18
5PCH(CP5CN)		Cr 30 N 55 I	0.12
6CHBT(CP6NCS)		Cr 13N 42.8 I	0.15

in the open atmosphere. The LC sample was placed in a glass vial of 1 cm diameter. The UV light Hamamatsu, (model L8868-01) was delivered through a fibre bundle and collimated by a lens. The output light passed through a narrow band interference filter centred at $\lambda=365$ nm. The lens was set at ~10 cm from the top of the LC surface; inside the sample, the UV light was relatively collimated. To ensure that the sample was exposed uniformly, a magnetic stirrer was used to agitate the LC molecules. The UV intensity at the sample position was measured to be $I \sim 150\,\mathrm{mW\,cm^{-2}}$. Every hour, a small amount of sample was removed from the container and its electro-optic property changes monitored. At the final stage of the experiment, the UV absorption was measured. We then dissolved each LC compound in a UV-transparent cyclohexane solution. To avoid detector saturation, the LC concentration was controlled at $2 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$. We used a dual channel Cary 500 UV spectrophotometer and 1 mm thick standard quartz cells for UV measurements.

For the electro-optic study, we monitored the changes in clearing temperature (T_c), birefringence (Δn), dielectric constants ($\varepsilon_{\|}$, $\varepsilon_{\perp}$), elastic constant (K_{11}, K_{33}) and visco-elastic coefficient (γ_1/K_{11}). To determine T_c, we used differential scanning calorimetry (DSC; TA-100). Through DSC, the phase transition temperature could be measured accurately to the second decimal place. To monitor the LC birefringence degradation, we filled an 8 µm homogeneous cell (pretilt angle ~3°) with the exposed LC and measured its phase retardation (δ). At a given temperature, the phase retardation is related to cell gap d, birefringence Δn, and wavelength λ by the relationship: $\delta=2\pi d\Delta n/\lambda$ [9]. All the measurements were performed using a He-Ne laser ($\lambda=633$ nm) at $T=23°C$. The dielectric and elastic constants of the three compounds were measured by the capacitance method [10] of a single homogeneous cell, using a computer-controlled Displaytech APT III instrument. We also measured the birefringence of the three LC compounds as a function of reduced temperature, defined as (T/T_C), in order to compare their performances.

3. Results and discussions

3.1. *UV absorption spectra*

The UV absorption spectra of a LC compound depend on its conjugation length [11]; both the core and the terminal group make contributions to this molecular conjugation length. Compounds 5PCH and 6CHBT have the same core structure (cyclohexane–phenyl rings), but their terminal groups are different; 5PCH has CN and 6CHBT has NCS. Figure 1 shows the UV absorption spectra of the three LC compounds, measured in a 2×10^{-4} molar cyclohexane solution. The two major $\pi \rightarrow \pi^*$ transitions [12,13] of 5CB appear at λ_1 ~200 nm and λ_2 ~275 nm, the tail ending at ~310 nm. Due to the effect of the solvent, the measured λ_2 is about 5 nm shorter than that measured in a pure thin LC cell. In the NCS compound 6CHBT,the λ_1 and λ_2 bands are each split into two closely overlapped bands. Due to the weaker oscillator strength, its Δn is slightly smaller than that of 5CB, as listed in the table. On the other hand, 5PCH has a shorter molecular conjugation so that its λ_2 occurs at ~235 nm, which is shorter than that of 5CB and 6CHBT. As a result, its birefringence is the smallest among the three compounds compared.

We compared the UV absorption spectra of these fresh compounds with those of samples already exposed to UV. The λ_2 absorption peak of 5CB is increased

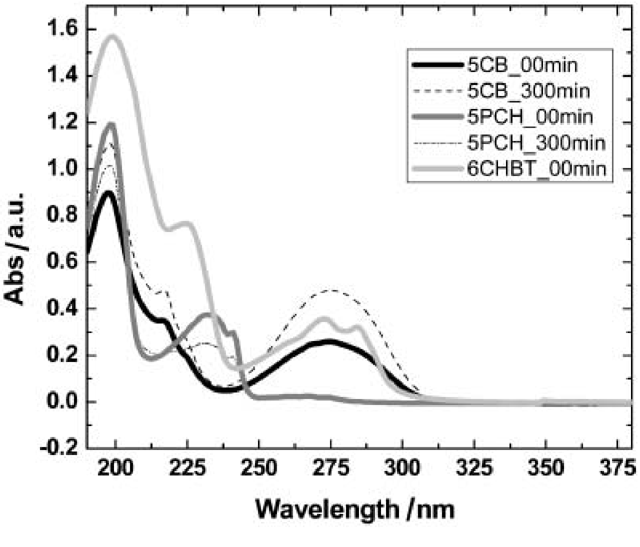


Figure 1. UV absorption spectra of 5CB, 5PCH and 6CHBT. Each LC compound was dissolved in cyclohexane at a concentration of $2 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$; 1 mm thick standard quartz cells were used for measurements.

from 0.26 to 0.48, while the λ_1 increased from ~0.897 to ~1.113. On the other hand, the λ_2 peak of 5PCH is decreased from ~0.375 to ~0.252 and the λ_1 from ~1.190 to ~1.011.

3.2. *Clearing temperature*

The nematic to isotropic phase transition temperature (T_c) of the three compounds were measured by DSC after each UV exposure period; the results are shown in figure 2. If a compound structure is altered by the UV photons, its phase transition temperature will change. Basically, we can measure their melting and clearing temperatures, but only the clearing temperature is needed to indicate the change caused by UV illumination. In figure 2, we find that the T_c of 5CB and 5PCH starts to decrease after the first hour of illumination and decreases further as the exposure time increases. After 5 h of exposure, the T_c of 5CB and 5PCH is decreased by 3.72 and 3.14°C, respectively, from the original samples. On the other hand, the T_c of 6CHBT, which has the NCS terminal group instead of CN, had only a minor change of 0.33°C

3.3. *Birefringence*

The birefringence of the three compounds was measured after every illumination period. The results are shown in figure 3. The birefringence of 5CB and 5PCH is reduced by 11 and 7%, respectively, after 5 h of UV illumination. By contrast, the birefringence of 6CHBT remains the same after 5 h of UV exposure.

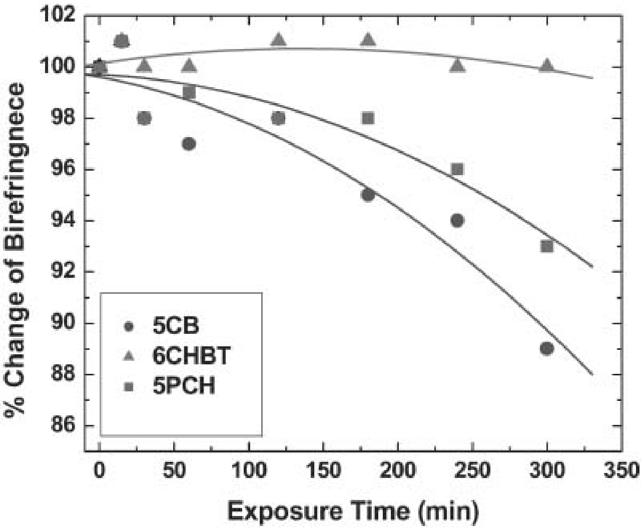


Figure 3. Change of birefringence as a function of UV exposure time. Triangles, squares and circles denote 6CHBT, 5PCH and 5CB, respectively. UV intensity $I = 150\,\mathrm{mW\,cm^{-2}}$, and the wavelength of measurements is $\lambda = 633\,\mathrm{nm}$.

In order to compare the performance of the three compounds, we measured birefringence at different temperatures. The results of birefringence as a function of reduced temperature are shown in figure 4. As indicated in this chart, 5CB shows the highest birefringence, exceeding those of 6CHBT and 5PCH. This high birefringence of 5CB arises from two phenyl rings instead of one, as in 6CHBT [14]. The difference in birefringence between 5CB and 6CHBT is only 0.05 at the reduced temperature $T_r = 0.9$.

The voltage-dependent transmittance before and

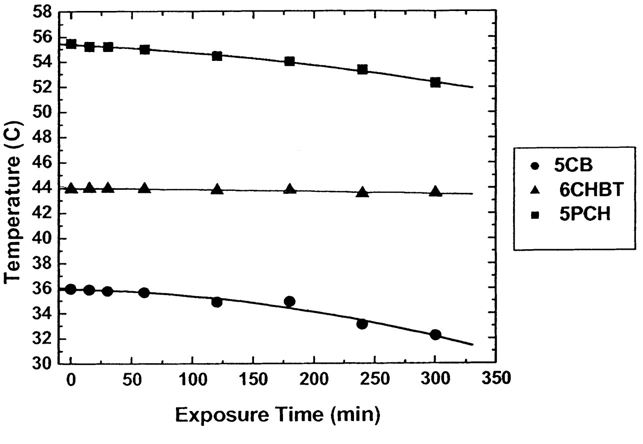


Figure 2. Clearing temperature (°C) as a function of exposure time. UV intensity $I = 150\,\mathrm{mW\,cm^{-2}}$. Triangles, squares and circles denote 6CHBT, 5PCH and 5CB, respectively.

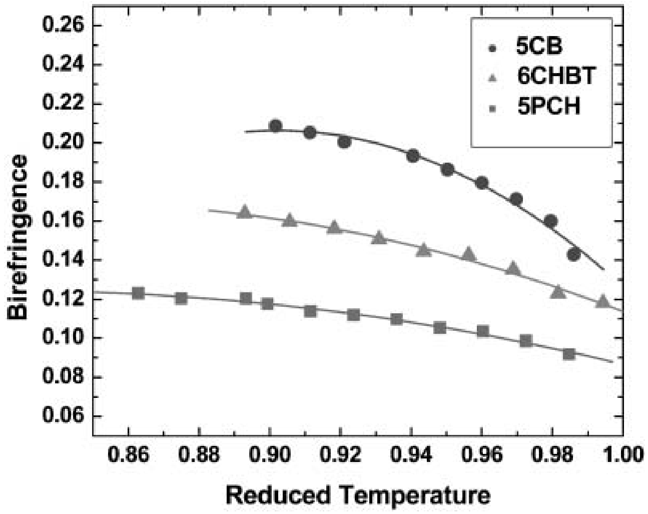


Figure 4. Birefringence as a function of reduced temperature (T/T_c). Circles, triangles and squares denote 5CB, 6CHBT and 5PCH, respectively.

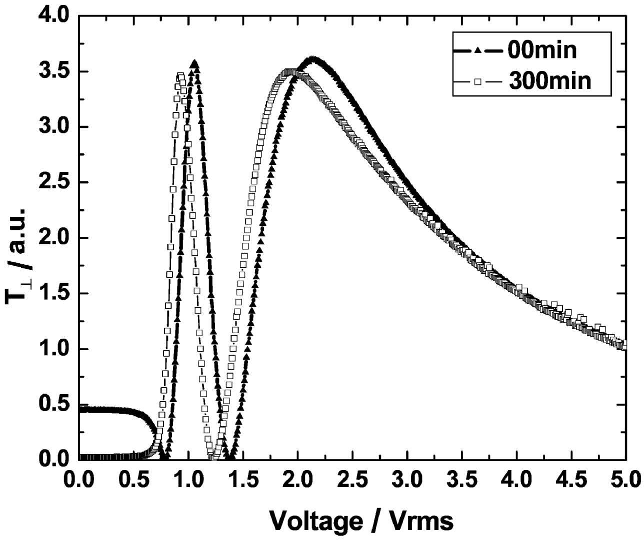


Figure 5. The voltage-dependent transmittance of 5CB. The transmittance was measured using a homogeneous cell between two crossed polarizers at $\lambda = 633\,\mathrm{nm}$. Solid triangles and open squares are data before and after UV exposure, respectively. UV intensity $I = 150\,\mathrm{mW\,cm^{-2}}$; the alignment layer was buffed polyimide film.

after UV exposure of these three compounds was monitored, with results shown in figures 5, 6 and 7. Several phenomena were observed in 5CB and 5PCH as degradation gradually took place: the effective Δn was decreased and light scattering was gradually increased [15].

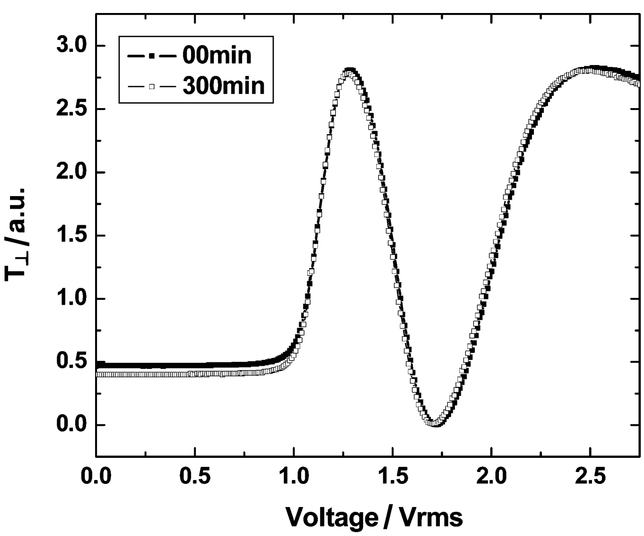


Figure 6. The voltage-dependent transmittance of a homogeneous LC cell containing 6CHBT. Experimental details are the same as for figure 5.

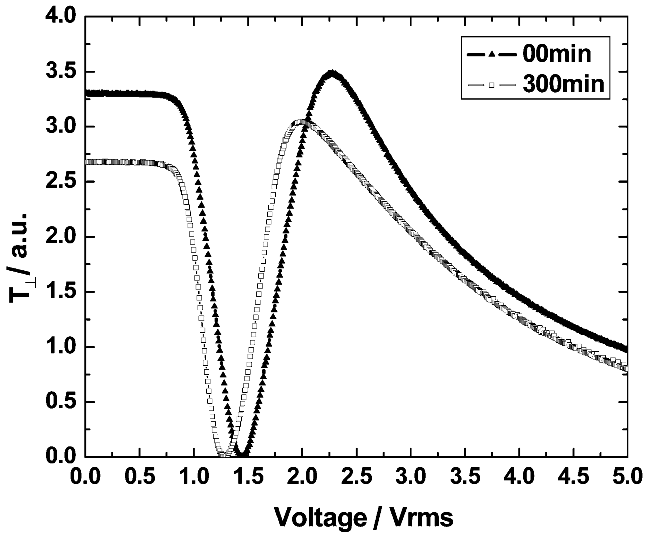


Figure 7. The voltage-dependent transmittance of a homogeneous LC cell containing 5PCH. Experimental details are same as for figure 5.

3.4. *Dielectric constants*

Since the dielectric anisotropy of a liquid crystal is $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, it is interesting to know the tendency of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ to change during UV illumination, in order to know the stability of the LCs. Here, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants along and perpendicular to the principal molecular axis, respectively. Figure 8 represents the percentage change of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of the exposure time. We find the $\varepsilon_{\parallel}$ of all three compounds changes only slightly (less than 2%) during

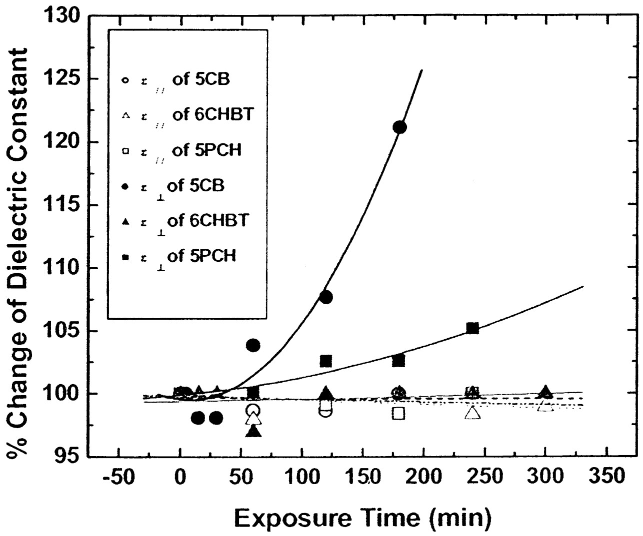


Figure 8. Dielectric constant as a function of exposure time. UV intensity $I = 150\,\mathrm{mW\,cm^{-2}}$. Dashed and solid lines represent $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, respectively.

the UV illumination; but $\varepsilon_\perp$ of 5CB and 5PCH tends to increase, especially 5CB. The $\varepsilon_\perp$ of 5CB is increased by 20% after 3 h of illumination; in contrast, the $\varepsilon_\perp$ of 6CHBT does not change, even after 5 h of UV illumination.

As we know, the dielectric constants of the anisotropic liquid crystals depend on the dipole moment and its orientation angle with respect to the principal molecular axis. If a compound is degraded due to UV irradiation, then its pretilt angle in a LC cell could be increased. As a result, the measured effective $\varepsilon_\perp$ is increased and the threshold behaviour is smeared. From figure 8, it can be seen that the molecular structures of 5CB and 5PCH have been altered during the UV illumination time, but 6CHBT remains the same. The degradation mechanism could originate from the electron cloud shift which is induced by the UV. Once these degraded LC compounds were filled into cells, their pretilt angle was enlarged resulting in increased $\varepsilon_\perp$.

3.5. *Elastic constants*

Elastic constant [16] is another quantity used to describe the restoring force after removing the external field. A closer view of the intermolecular forces is obtained by measuring $K_{11}$and K_{33}. Figure 9 shows the percentage change of K_{11} and K_{33} as a function of the UV exposure. The K_{11} of all three compounds changes only minimally, but the K_{33} of 5CB and 5PCH decreases to 40% and 50%, respectively. Since K_{11} and K_{33} represent the restoring force in different directions in a liquid crystal cell, we separate the intermolecular force into two directions. One is the interaction between the long sides of molecules, the other is the interaction between the head and tail of molecules, as shown in figure 10.

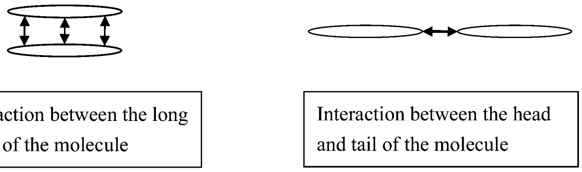


Figure 10. Two different kinds of molecular interaction in a liquid crystal cell.

The stable K_{11} indicates that for all three compounds the intermolecular force does not change between the long sides of the molecular axis. On the other hand, the large decrease in K_{33} implies that the molecular structures of 5CB and 5PCH are changed after UV exposure. By combining the K_{33} properties with the UV absorption spectra, we found that the UV changed the structure of the terminal group of 5CB and 5PCH, but not of the phenyl ring.

Figure 11 shows the γ_1/K_{11} of all three compounds as a function of UV exposure time. Since K_{11} does not change from the previous measurement, the increment of γ_1/K_{11} in 5CB comes from the increased viscosity.

3.6. *Physical mechanisms*

From the molecular structure standpoint, 5PCH has the shortest conjugation, followed by 6CHBT and then 5CB. However, the UV stability has the following order: 6CHBT >5PCH >5CB. This is different from our expected order of 5PCH >6CHBT >5CB, judged from their absorption spectra. The reversed stability order between 6CHBT and 5PCH indicates that the NCS terminal group is more UV resistant than CN.

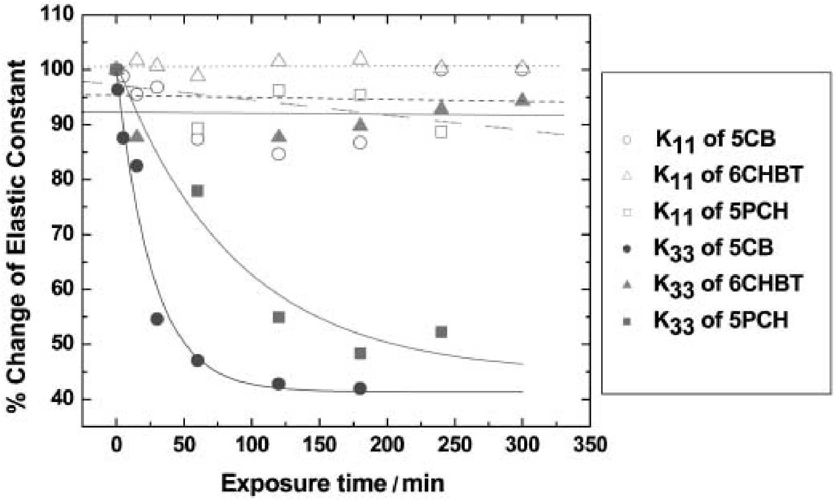


Figure 9. Elastic constant as a function of exposure time. Experimental details are same as for figure 8.

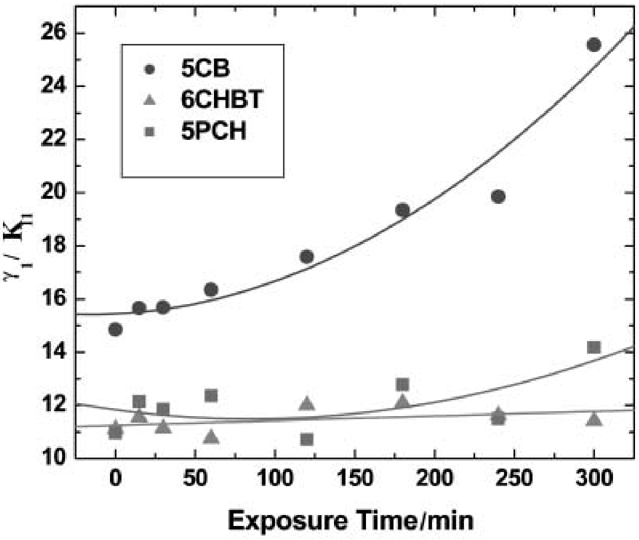


Figure 11. γ_1/K_{11} as a function of exposure time. Experimental details are same as for figure 3.

By considering the Lewis structure [17], which shows the electron distribution of the molecule, both CN and NCS have a resonance structure, corresponding to electron delocalization over the molecule. The more resonance contributors there are, the more stable is the molecule, because of the better sharing of electrons. Figure 12 shows the Lewis resonance structure of NCS^{-1} and CN^{-1}[17, 18]. Since NCS has one more resonance component than CN, the electron delocalization is more stable in NCS than in CN. These resonance structures explain why NCS is more stable than CN. However, our compounds have an additional phenyl ring. Thus, we have to consider the conjugated structure of CN or NCS with a phenyl ring.

Figure 13 shows the molecular structure of a phenyl ring with a CN terminal group (Ph-CN) [19]. Since nitrogen has an unshared electron pair and CN is an electrophile [17], the aromatic ring supplies two electrons to form a covalent bond with the carbon atom, causing a temporary electron deficiency which is accommodated in the π-orbitals of the residual aromatic system [20]. In contrast, NCS is a nucleophilic substituent, and two electrons are supplied for the formation of the new bond by the unshared electrons of the nitrogen atom; the phenyl ring then accommodates a negative charge and forms a very stable resonance structure [21]. Therefore, a phenyl ring with a nucleophilic substituent will form a more stable resonance structure than one with an electrophilic substituent. That is to say, 6CHBT will exhibit a better UV stability than 5PCH, as observed in our experiment.

Since our UV exposure was conducted in normal atmosphere, oxidations of 5CB and 5PCH were detected from the infrared absorption change. No such evidence was found in 6CHBT. Since CN is less stable than NCS, cyano compounds are more easily damaged by UV. The oxidation process takes place at an earlier stage which leads to the macroscopic degradation of the observed electro-optic properties.

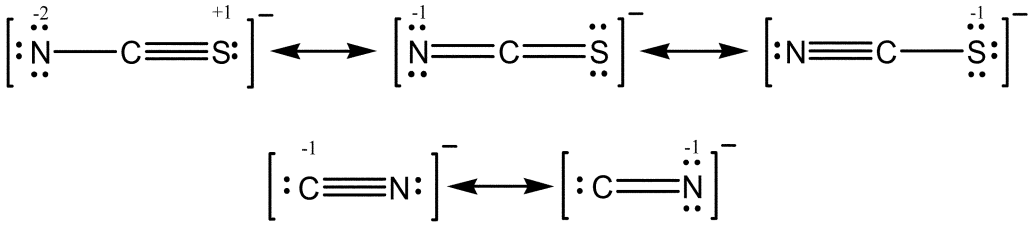


Figure 12. Lewis resonance structure of NCS and CN.

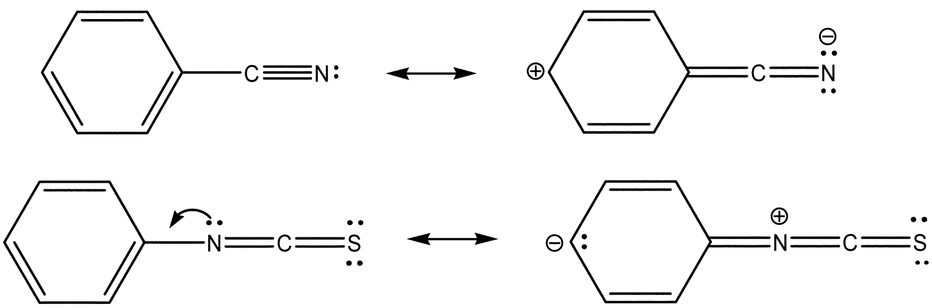


Figure 13. Lewis resonance structure of Ph-NCS and Ph-CN.

4. Conclusions

We have studied the UV stability of three similar structures with CN and NCS terminal groups. Even though they have similar conjugation lengths, the NCS compound exhibits a better UV stability than the CN compound at 365 nm UV exposure. To explain this, we find that the NCS group has a better electron delocalization than the CN group. The resonance structures also show that phenyl-NCS conjugation is more stable than phenyl-CN conjugation. This is because NCS is a nucleophilic substituent. In addition, the NCS compounds possess a higher birefringence and a lower viscosity than the corresponding CN compounds. More extensive applications of NCS compounds may therefore be foreseen.

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