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# Azo Monomers Exhibiting Low Layer Shrinkage at the SmA–SmC Transition and *trans–cis* Light-Induced Isomerization

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Methacrylic monomers containing a (phenylene)azobenzene unit substituted with a lateral cyano group and alkyl chains of different length are synthesized and characterized by NMR techniques. Their liquid-crystalline properties are studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. All monomers exhibit a mesomorphic behavior that extends over wide temperature ranges with nematic and orthogonal or tilted smectic-type mesophases, depending on the length of the terminal chain. The smectic structures are determined to be single-layered with a low layer shrinkage (< 5%) at the SmA-SmC transition. This atypical behavior is at-

# tributed to the combination of a high smectic order promoted by both $\pi$ - $\pi$ and bond dipole–bond dipole interactions between cyano-substituted central cores, and a low correlation between neighboring layers arising from dispersive forces between the end groups (methacrylic group and alkyl chain) of the monomer. On the other hand, the *trans-cis* isomerization of monomers is induced in solution by irradiating with a UV lamp. High *cis*-isomer contents ( $\geq$ 96%) are obtained at the photostationary state, which is reached in a relatively short time (40 s).

# 1. Introduction

Azobenzene liquid crystals combine two physical properties of practical interest: the spontaneous self-organization of molecules in mesomorphic states and the reversible photoinduced trans-cis isomerization of the azo group.<sup>[1-3]</sup> Such coexistence can produce a significant synergistic effect in properties, for instance in the light-induced birefringence of films irradiated with linearly polarized light.<sup>[4,5]</sup> It turns out that the liquid-crystalline (LC) order improves the photoinduced alignment of azobenzenes through a coordinated motion of molecular domains, and also stabilizes it once the light is turned off,<sup>[6]</sup> although the trans-cis conformational switching could affect or disrupt the LC order.<sup>[7,8]</sup> In this concern, much investigation has been conducted on side-chain LC polymers with the azo chromophores as pendant groups.<sup>[9-11]</sup> There are several ways in which the azo chromophore can be inserted into a polymer chain, and the simplest one is probably by polymerizing monomers bearing this group.<sup>[12,13]</sup> Some of these "azo monomers" are liquid crystals and their photoisomerization in a mesomorphic state has been used to enhance the molecular alignment.<sup>[13,14]</sup> This strategy avoids the use of prealigned substrates and/or the application of rubbing or some other surface treatment that promotes molecular orientation in a preferential direction,<sup>[15,16]</sup> and also allows the bulk alignment through the action of the photoactive azobenzene moieties.<sup>[17]</sup>

There is a kind of liquid crystal known as "de Vries material" that shows low or no layer shrinkage at the smectic A to smectic C (SmA–SmC) transition. This behavior arises from the fact that the tilt angle of molecules in a smectic A phase is already large, and no further inclination occurs in the transition to a smectic C phase but only a molecular reorientation. This singular phenomenon has become an important problem in the theory of liquid crystals and a key issue for applications in which a minor layer contraction in externally induced molecular reorientations is desired.<sup>[18]</sup> Theoretical and experimental evidence on de Vries-like materials is extensively documented elsewhere.<sup>[19,20]</sup>

Most de Vries liquid crystals have been characterized by X-ray diffraction (XRD) to validate the unusual, small variation of the smectic period (*d*) at the SmA–SmC transition.<sup>[21]</sup> Such a small variation of *d* was first explained by Adrian de Vries himself through a "diffuse cone model" in which molecules in a smectic A phase are tilted in a random distribution in azimuthal directions, whereas in a smectic C phase the molecules reorient into a specific azimuthal direction; as the average tilt angle is similar in both phases, no layer contraction occurs in the transition from one phase to the other.<sup>[22]</sup> Some other experimental techniques such as nuclear magnetic resonance (NMR) spectroscopy have recently been used to characterize de Vries-like liquid crystals. By this technique an average tilt angle of molecular moieties in the SmA phase was confirmed.<sup>[23]</sup> Also, a strong magnetic effect on the orientational

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order of the aromatic core within the stability region of the SmA phase was observed. From these observations a variation of the diffuse cone model was proposed, which consisted of smectic layers with locally ordered distribution of molecules in azimuthal directions, namely the cluster diffuse model.<sup>[24]</sup> In the present study, XRD results, coupled with microscopic optical observations, and supported by unperceived differential scanning calorimetry (DSC) enthalpies at the SmA–SmC transition, let us determine a de Vries-like behavior in the studied monomers.

The simple reorientation of molecules at the SmA-SmC transition in de Vries-like liquid crystals is advantageous for practical applications. For instance, high electroclinic effects (response, tilt angle, and birefringence) can be achieved at low voltages as compared with typical electroclinic materials.<sup>[25,26]</sup> Furthermore, the low layer contraction avoids the formation of a chevron structure and zigzag defects that usually occur in SmA-SmC transitions of conventional ferroelectric (SmC\*) liquid crystals and that are detrimental for the optical quality of electro-optical devices. The reorientation of molecules is also interesting in de Vries LC elastomers, the low birefringence value of which arises from the high tilt angle of molecules (randomly oriented in azimuthal directions) in the smectic A phase.<sup>[27]</sup> Under strain, the correlation in tilt alignment could be extended, thus allowing the elastomer to deform at low energy cost. Compared to a classical elastomer, a de Vries elastomer would display large birefringence under minor stress. For azo polymers the light-induced isomerization changes the shape of mesogens from rodlike to kinklike, thereby destabilizing the LC order.<sup>[28]</sup> The concept was transferred to LC elastomers to produce contraction, expansion, and/or bending by irradiation at constant temperature. The reisomerization of the azo groups makes the actuation reversible. All these characteristics in a single molecule open up the scope to explore both new properties and potential applications.

Molecules with different composition and geometry, such as chiral smectic materials and smectic liquid crystals bearing highly segregating elements (e.g. siloxane and fluorinated tails), have been reported to show a low layer-shrinkage behavior.<sup>[29,30]</sup> To the best of our knowledge, there is only one report due to González-Henríquez et al. on monomers showing no interlayer contraction at the SmA–SmC transition.<sup>[31]</sup> It concerns methacrylic monomers bearing an azobenzene unit, substituted with one lateral OH group and two alkyl chains at the 4- and 4'-positions. It was stated that for a smectic A phase of de Vries-like materials there may exist a high lamellar order, with both a low orientational correlation of molecules within layers and a weak coupling between layers.<sup>[22]</sup> The presence of

highly segregating elements such as those mentioned above helps to satisfy such conditions, although there are some exceptions to this unwritten rule. In the already mentioned monomers only weak segregating elements are present and they are probably associated with the low layer-shrinkage behavior. We have synthesized a series of methacrylic monomers bearing a cyano-substituted (phenylene)azobenzene core that also exhibits a low layer shrinkage at the SmA-SmC transition. These monomers without highly segregating groups show some structural similarities to those reported by González-Henríquez et al., and herein we propose that their de Vries-like behavior arises from comparable chemical interactions. The photoinduced properties of these azo monomers are also presented and discussed.

# 2. Results and Discussion

### 2.1. Synthesis

Monomers were prepared as reported previously.<sup>[32]</sup> In the present work, only the last reaction is shown (Scheme 1), which consists of the esterification of methacrylic acid with a bromoalkyl derivative. All bromoalkyl derivatives (here named mesogens) have shown interesting LC properties and for this reason they were included for discussion. Monomers and mesogens have a (phenylene)azobenzene unit substituted with a lateral CN group. In these molecules the terminal chain has 6, 10, or 12 carbon atoms, whereas the "spacer" has six methylene groups. These monomers were named Mon6, Mon10, and Mon12 and their corresponding mesogens Mes6, Mes10, and Mes12.

### 2.2. NMR Characterization

Monomers and mesogens here synthesized were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. This full characterization was necessary taking into account that some authors differ in the assignment of hydrogen atoms in similar azobenzene cores.<sup>[33,34]</sup> <sup>1</sup>H, <sup>13</sup>C, COSY (H–H COrrelation SpectroscopY), HMQC (C–H Heteronuclear Multiple Quantum Correlation), and HMBC (C–H Heteronuclear Multiple Bond Correlation) NMR techniques allowed us to assign unequivocally the chemical shifts to the whole molecule. For the sake of simplicity, here only the <sup>1</sup>H and <sup>13</sup>C NMR spectra of one mesogen (Mes6) were selected for discussion (Figure 1). The chemical shifts ( $\delta$ ) and coupling constants ( $^{T}$ <sub>J–H</sub>) are expressed in terms of ppm and hertz, respectively. Signals of the aromatic hydrogen atoms H2, H16, H19; H15, H20, and methylene groups 8, 22, and 27 alpha



Scheme 1. Last step in the synthesis of mesogens and monomers bearing a (phenylene)azobenzene unit substituted with a CN lateral group. HQ = hydroquinone.

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Figure 1.  $^1\!H$  NMR spectrum (A) and  $^{13}\!C$  NMR spectrum (B) of the mesogen Mes6.

to two oxygen and bromine atoms showed first-order pattern coupling as described below.

The fairly good resolution of the <sup>1</sup>H NMR spectrum of Mes6 (Figure 1 A) let us distinguish seven signals in the aromatic region, which correspond to seven chemically different protons out of a total of 11 aromatic hydrogen atoms. The two doublet-like signals centered at  $\delta =$  7.95 (d,  ${}^{3}J_{\rm H20-H19} =$  8.5 Hz) and 7.92 ppm (d,  ${}^{3}J_{H15-H16}$  = 8.8 Hz) correspond to H19 and H16 located in the ortho position to the azo group. The signal centered at  $\delta = 7.82$  ppm was assigned to H5 (d,  ${}^{4}J_{H_{5}-H_{3}} = 2.2$  Hz). The doublet of doublets centered at  $\delta =$  7.77 ppm and coupled with H2 and H5 (dd,  ${}^{3}J_{H3-H2} = 8.8$ ,  ${}^{4}J_{H3-H5} = 2.4$  Hz) was attributed to H3. The doublet centered at  $\delta =$  7.62 ppm and coupled with H16 (d,  ${}^{3}J_{H15-H16}$  = 8.5 Hz) was assigned to two equivalent H15 hydrogen atoms. Finally, signals at  $\delta =$  7.02 (d,  ${}^{3}J_{H2-H3} =$  8.8 Hz) and 7.00 ppm (d,  ${}^{3}J_{H20-H19} = 9.0$  Hz) correspond to H2 and to two equivalent H20 hydrogen atoms, respectively. H2 and H20 are shifted towards the lowest frequencies of the aromatic region due to mesomeric effects by oxygen atoms. Note that all experimentally observed chemical shifts concur with those calculated by a theoretical simulation of the <sup>1</sup>H NMR spectrum (ACD-Labs software). In the middle part of the <sup>1</sup>H NMR spectrum three triplets are clearly distinguished: those centered at  $\delta = 4.10$  (t,  ${}^{3}J_{\text{H8-H9}} = 6.4$  Hz) and 4.04 ppm (t,  ${}^{3}J_{\text{H22-H23}} = 6.3$  Hz) correspond to the methylene groups alpha to the oxygen atom (H8 and H22, respectively), and that centered at  $\delta = 3.43$  ppm corresponds to the protons H27 (t,  ${}^{3}J_{\text{H27-H26}} = 6.4$  Hz) of the methylene group alpha to the bromine atom. All aliphatic hydrogen atoms located in the low-frequency region of the spectrum (between  $\delta = 0.9$  and 2.0 ppm) were assigned through the combination of the NMR techniques described in the Experimental Section. For more details refer to the Supporting Information.

The <sup>13</sup>C NMR spectrum (broad band decoupling) shows 27 out of a total of 31 signals expected for Mes6, which means that four carbon-atom pairs are chemically equivalent (Figure 1B). Such carbon-atom pairs (C15, C16, C19, and C20) are those in close vicinity to the C14-C4 and C18-N bonds. The two signals located at the highest frequencies of the spectrum correspond to C21 ( $\delta\!=\!$  161.8 ppm) and C1 ( $\delta\!=\!$  160.47 ppm), and are affected by the inductive effect of the corresponding oxygen atoms. The signal at  $\delta = 116.3$  ppm, which corresponds to C7 (cyano group) and is assigned by HMBC (see Supporting Information), showed a three-bond distance correlation with H5. The quaternary carbon atoms C21, C1, C17, C18, C14, C4, and C6 were also unequivocally assigned by means of HMBC. From  $\delta =$  33.7 to 14.0 ppm the spectrum shows ten signals corresponding to all the carbon atoms of the aliphatic chains, except those alpha to the oxygen atoms. C11 and C12 were not possible to assign by HMBC, but by means of steric and inductive effects of their corresponding neighbors in the alpha and beta positions.[35]

#### 2.3. Thermal Properties

All synthesized monomers and mesogens were first analyzed by thermogravimetric analysis (TGA) and the obtained results are shown in Table 1. It can be noticed that for monomers the initial decomposition temperature ( $T_{5\%}$ ) is located between 313 and 324 °C, whereas for mesogens it is between 254 and 260 °C. The thermal stability of mesogens is much lower than that of monomers, probably due to the low dissociation energy of the Br–C bond.<sup>[36]</sup> The  $T_{5\%}$  is well above the clearing point for all molecules, thus assuring that no decomposition occurs during their thermotropic examination.

The thermotropic behavior of monomers and mesogens was first studied by DSC in both heating and cooling scans, and thermograms showed at least two first-order thermal transitions. The DSC curves of both mesogens and monomers are grouped in Figure 2. It can be seen that each monomer displays a similar polymorphic behavior to its mesogen counterpart. The only difference is the temperature at which thermal transitions occur, which is in general lower for monomers. In both monomers and mesogens the transition from the LC to the crystal state is lacking, which suggests long induction periods for crystallization. To see the melting endotherm in the DSC traces, samples were run (second heating) for several hours after the first cooling.

Compound	L [Å]	<i>Т</i> [°С]	d [Å]	d/L	Tilt angle <sup>[a]</sup> [°]	Τ₅% [°C]	Mesophase <sup>[b]</sup> (enthalpy) [°C (kJ mol <sup>-1</sup> )]
Mes6	34.2	140	32.2	0.94	19.7	254	SmA147 (0.29) N160 (0.70) l
Mon6	36.6	120	34.9	0.95	17.5	313	SmA140 (0.47) N144 (0.48) l
Mes10	39.2	140	36.0	0.92	23.3	256	SmA150 (3.68) l
Mon10	41.6	80	36.8	0.89	27.8	318	SmC95
		120	37.8	0.91	24.7		SmA132 (3.75) l
Mes12	41.7	120	38.7	0.93	21.9	260	SmA151 (3.50) l
Mon12	44.1	80 120	40.7 39.9	0.92 0.91	22.6 25.2	324	SmC105 SmA133 (3.02) I

DSC traces remained unchanged at such temperatures. Undetectable or almost imperceptible DSC enthalpies have been reported in some other works on liquid crystals. For instance, in studying semi-perfluorinated alkyl chain-substituted terphenyl molecules, Ishida et al. reported a SmA to SmC transition from optical observations at variable temperature; the enthalpy change for this transformation was too small to be detected in DSC thermograms.[38]

The nature of the observed LC phases was determined by XRD



Figure 2. DSC thermograms (heating and cooling scans) of monomers and mesogens.

## 2.4. Structure of Mesophases

isotropic.

Monomers and mesogens were studied by polarizing optical microscopy (POM) at variable temperature, first to corroborate the DSC results and second to obtain and analyze the optical texture of each mesophase. From all the micrographs captured upon cooling, only a few of them were selected as representatives of these materials (Figure 3).

All samples exhibited focal-conic fan (Figure 3 A, B) and homeotropic (Figure 3 C) textures, typical of smectic phases. Only the shortest ones (Mon6 and Mes6) develop an additional lowviscosity schlieren texture of a nematic phase (Figure 3 D). The presence of a nematic phase is common in liquid crystals containing short flexible chains, as was reported for many homologous series including those having an azobenzene group.<sup>[37]</sup> It is worth mentioning that an unexpected optical transition was observed for the monomers with a longer tail. For Mon10, a homeotropic to a sanded texture transition was detected around 95 °C (Figure 4 A, B), whereas for Mon12 the smooth fanshaped texture developed at high temperature was transformed around 100 °C into a broken fan-shaped texture with a sanded appearance (Figure 4 C, D). This change suggests a phase transition despite the fact that in both monomers the analysis. Only nematic and nonordered smectic phases were found by this technique. The nematic phase was determined



**Figure 3.** Focal-conic fan texture of Mes10 at 149 °C (A) and Mes6 at 120 °C (B), homeotropic texture of Mon6 at 135 °C (C), and gray schlieren texture of Mon6 at 141.6 °C (D).



**Figure 4.** Homeotropic texture with residual "bâtonnets" at 133 °C (A) and sanded texture at 95 °C of Mon10 (B). Focal-conic fan texture at 120 °C (C) and broken fan texture at 100 °C of Mon12 (D).

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for the monomer Mon6 and the mesogen Mes6, which displayed no sharp reflection while being birefringent at high temperature (schlieren texture by POM). On the other hand, the smectic phases were determined from the sharp Bragg reflection appearing in the low-angles region of the XRD patterns (Figure 5). Such reflection is related to the interlayer distance (*d*) of the lamellar structure.



Figure 5. XRD patterns of monomers and mesogens captured at 120  $^\circ\text{C}$  upon cooling.

To determine the way the molecules are arranged within the lamellar structure, the experimental interlayer distance was compared with the length of the molecule in its most extended conformation (*L*) calculated by molecular modeling software (Spartan 2010) and the resulting d/L ratios are presented in Table 1. For both monomers and mesogens the calculated d/L values are close to unity, which suggests a single-layer packing with molecules oriented on average perpendicular to the smectic plane.

The smectic phases were definitely recognized from the analysis of the wide-angle region of the X-ray patterns (Figure 5). In this region, all molecules developed only one broad Bragg reflection centered around 22°, which is indicative of a liquid-like ordering of molecules within the smectic layers as occurs in SmA or SmC phases. As mentioned above, none of the molecules showed a crystallization exotherm by DSC (Figure 3); however, a clear spherulitic growth was perceived

by POM in some of them, probably promoted by a shear-induced flow orientation occurring between parallel glass plates. The wide-angle region of the Xray patterns registered at room temperature also confirms the crystallization of molecules, as shown for Mon12 in Figure 6.



Figure 6. XRD patterns of Mon12 captured at different temperatures upon cooling.

The exact nature of the mesophases of each of the monomers and mesogens was determined from the combination of DSC, POM, and XRD results. Nematic and single-layer SmA and SmC phases were the only observed mesophases (Table 1). As is known, molecules in a SmA phase are on average perpendicular to the smectic plane, although a close inspection of the calculated d/L ratios indicates that molecules are somewhat tilted ( $\cos^{-1} d/L = 17.5 - 25.2^{\circ}$ ). On the other hand, molecules in a SmC phase are tilted, but for Mon10 and Mon12 the tilt angle is rather weak ( $\cos^{-1} d/L = 27.8$  and  $22.6^{\circ}$ , respectively). In terms of tilt angle there is not a sharp borderline between SmA and SmC phases, but an undefined region. For the SmA and SmC phases of these monomers the measured tilt angle is close to (or within) such a region. Therefore, on cooling from one phase to the other one might expect a minor change in the interlayer distance (by XRD) and a low enthalpic transition (by DSC), as actually observed for the monomers Mon10 and Mon12. For the vast majority of liquid crystals the SmA-SmC phase transition is accompanied by a significant contraction of the interlayer distance (around 7-10%).<sup>[18]</sup> For de Vries-like liquid crystals the minor layer contraction (less than 1%) is normally explained through an idealized diffuse cone model (Figure 7) consisting in the ordering of the random azimuthal distribution of tilted molecules within the smectic layers that results in no or low layer contraction.<sup>[22]</sup> Molecules showing contractions between 1 and 5% at the SmA-SmC transition were also classified as de Vries materials. Roberts et al. reported 1.6-4.2% for pyrimidinol-trisiloxane derivatives,<sup>[22]</sup> whereas Ishida et al. reported values of around 2% for amphiphilic liquid crystals bearing semi-perfluorinated chains.<sup>[38]</sup> Podoliak



Figure 7. Model for a SmA–SmC transition with a minor change in the interlayer distance (d).

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et al. reported a chiral liquid crystal bearing an azobenzene group in which the layer contraction is about 4%.<sup>[39]</sup>

To assess the de Vries character of Mon10 and Mon12, the  $d/d_{AC}$  ratios were determined each 5 °C in the reduced temperature of  $T - T_{AC} = -80 \,^{\circ}\text{C}$  ( $d_{AC}$  and  $T_{AC}$  are the interlayer distance and the temperature at the SmA-SmC transition, respectively). The  $d/d_{AC}$  ratios were then plotted against  $T-T_{AC}$  (Figure 8A) to



Figure 8. Relative smectic layer spacing  $d/d_{AC}$  versus reduced temperature  $T-T_{AC}$  for Mon10 (**a**) and Mon12 (**b**) (A), and interlayer distance versus temperature for Mon6 (A) measured from small-angle X-ray scattering analysis (B).

characterize the interlayer contraction in the vicinity of the SmA-SmC transition. Both the overall feature of the resulting curves and the  $d/d_{AC}$  ratios higher than 0.95 confirm the de Vries-like behavior of Mon10 and Mon12. The gradual decrease in  $d/d_{AC}$ , which occurs from  $T_{AC}$  to  $T-T_{AC} = -30$  °C, indicates that the SmA-SmC transition is second order. The maximum layer contraction measured at  $T-T_{AC} = -30$  °C is 3.3 and 4.8% for Mon10 and Mon12, respectively. A strong negative thermal expansion is observed in both SmA and SmC phases. This effect is simply associated with an increase of both the orientational ordering and the effective length of molecules that continuously stiffens as the temperature decreases. The monomer Mon6 showed a typical behavior of a smectic phase whose interlayer distance steadily increased upon cooling due to such a negative thermal expansion effect (Figure 8B).

To our knowledge there is only one report on methacrylic azo monomers showing low layer-shrinkage behavior.<sup>[31]</sup> Such monomers have an azobenzene unit 4,4'-substituted with alkyloxy chains and a lateral OH group, the methacrylic monomer being attached to one of the chain ends. These monomers have no chiral or highly segregating elements as should be normal for typical de Vries-like materials, which according to theory might have a high lamellar order with low correlation between layers. These authors do not discuss the origin of the low layer shrinkage, but it can be argued that the lamellar ordering may arise from dispersing forces between the rigid rodlike aromatic groups (azobenzenes) and the alkyl chains. Such order seems to be reinforced by hydrogen-bonding interactions between the OH groups substituted in the central core. The end groups of these monomers (methacrylic group and

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alkyl chain) are not highly segregating elements, but they are incompatible enough with one another to weaken the coupling between neighboring layers. Our molecules share some structural characteristics with the already mentioned azo monomers, and therefore their low layer-shrinkage behavior may be explained in similar terms. The smectic order may arise from the incompatibility between the (phenylene)azobenzene core and the alkyl chains, but it seems to be reinforced by bond dipole-bond dipole interactions that may occur between CN groups. It is noteworthy that among the bond dipole moments one of the largest is that of the cyano group.<sup>[40]</sup> The (phenylene)azobenzene is a long rigid core that might develop strong  $\pi$ - $\pi$  interactions, which in turn may induce a high smectic order.<sup>[41]</sup> Sandhya et al. have reported a variety of de Vries-like molecules with not only chiral and highly segregating groups but also a long rigid core, as indeed is the case of many other compounds showing such a behavior.<sup>[42]</sup> The effect of the long rigid rodlike core was not examined in such compounds, but considering the large number of de Vries-like liquid crystals with a long aromatic group, one may perhaps consider it as a reinforcing element for a de Vries-like behavior.

Up to now, all reported de Vries-like materials have displayed upon cooling an isotropic (I)-SmA-SmC sequence. The absence of a nematic (N) phase is in fact considered as one of the essential conditions for de Vries behavior.<sup>[20]</sup> The monomers Mon10 and Mon12, which show a low layer shrinkage, displayed upon cooling an I-SmA-SmC sequence, whereas Mon6, which shows no de Vries-like character, displayed an I-N-SmA sequence. Thus, our results corroborate once again this essential condition.

Much work has been devoted to de Vries-like materials having different chemical structure. However, the structural characteristics of molecules inducing low layer shrinkage at the SmA-SmC transition are not yet fully understood. We hope this work will draw academic interest to design de Vries-like materials without highly segregating groups, which up to now have been scarcely explored.

## 2.5. Optical Properties

The light-induced properties of azo chromophores depend primarily on their capacity to photoisomerize under the effect of a specific light stimulus. In this section we present preliminary results on the light absorption characteristics as well as on the photochemical trans-cis isomerization kinetics of synthesized monomers and mesogens, irradiated in solution using spectrometric-grade THF as solvent.

The UV/Vis absorption spectra of monomers are similar to those of the corresponding mesogens. Also, the chain length has no effect on the UV/Vis absorption characteristics. For these two reasons only the spectrum of Mon12 was selected for discussion (Figure 9). Before irradiation (t=0 s), the trans isomer displays one strong absorption band centered at 368 nm and one weak band at 460 nm, associated with the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  electronic transitions, respectively.  $^{[41]}$  It can be seen that after irradiation at definite time intervals the intensity of the strong absorption band decreases to reach a photo-



**Figure 9.** UV/Vis absorption spectra of Mon12 obtained by photoisomerization at intervals of 10 s up to the photostationary state.

stationary state (PSS). This simply indicates that the more stable *trans* isomers are progressively transformed into the less stable *cis* isomers. For Mon12 the PSS was reached in only 40 s, thus showing high *cis*-isomer contents ( $\geq$  96%). The presence of neat isosbestic points in superposed UV spectra confirms that distinct absorbing species were in equilibrium with each other and that no degradation or side reactions took place during the photochemical isomerization experiments. For the other compounds similar results were obtained as shown in Table 2. Both the short PSS and the high *cis*-isomer contents obtained for all these molecules are promising for further studies on photoinduced properties.

Table 2. UV/Vis optical properties for mesogens and monomers.								
Compound	$arepsilon_{ m trans}^{[a]}$ [Lmol <sup>-1</sup> cm <sup>-1</sup> ]	λ <sub>max</sub> [nm]	PSS <sup>[b]</sup> [s]	% <i>cis</i> <sup>[c]</sup>				
Mes6	3.26×10 <sup>4</sup>	368	45	98				
Mon6	3.98×10 <sup>4</sup>	368	50	97				
Mes10	3.46×10 <sup>4</sup>	368	40	98				
Mon10	3.82×10 <sup>4</sup>	368	50	98				
Mes12	4.19×10 <sup>4</sup>	368	40	97				
Mon12	$4.23 \times 10^{4}$	368	40	96				
[a] Calculated from $A = \varepsilon lc$ at different concentrations. [b] Irradiation at								

366 nm until no change in absorbance is observed. [c] Calculated as in ref. [32].

# 3. Conclusions

Methacrylic monomers bearing a (phenylene)azobenzene core substituted with a lateral CN group were synthesized and characterized. These highly anisotropic molecules exhibit nematic and smectic-type LC phases in wide temperature ranges. The smectic phases were all single layered, and in some of the monomers low layer shrinkage in the SmA to SmC transition was observed, typical of de Vries-like liquid crystals. This behavior is probably associated with strong  $\pi$ - $\pi$  and bond dipole-bond dipole interactions between the cyano-substituted central cores that may induce a high smectic order, and also with dispersive forces of the methacrylic and alkyl chain end

groups. On the other hand, monomers photoisomerize in relatively short times and reach high *cis*-isomer contents ( $\geq$  96%).

# **Experimental Section**

Materials: Methacrylic acid, potassium hydrogen carbonate, and hydroquinone were purchased from Aldrich and used as received unless otherwise noted. Reactive grade solvents such as dimethylformamide (DMF), acetone, and chloroform were purchased from J. T. Baker or Aldrich and used without further purification. Mes6, Mes10, and Mes12 were prepared using the materials and procedures reported previously.<sup>[32]</sup>

Characterization: All intermediates and final molecules were characterized by <sup>1</sup>H, <sup>13</sup>C, COSY, HMQC, and HMBC NMR techniques, with CDCl<sub>3</sub> as solvent at 25  $^{\circ}$ C. <sup>1</sup>H and COSY spectra were obtained in a 300 MHz Jeol Eclipse spectrometer (using a 5 mm inverse broad band probe (BBI)), and <sup>13</sup>C, HMQC, and HMBC spectra in a 500 MHz Bruker Avance III instrument (using a 5 mm direct broad band with Z-grad (PABBO-1H/D Z-GRAD) probe, optimized for  ${}^{1}J_{C-H} = 145$  Hz and long range  $J_{C-H} = 8$  Hz). The chemical shifts in both <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual nondeuterated solvent. The thermal stability of vacuum-dried samples was examined in a thermal analyzer from DuPont Instruments (TGA 951) connected to a nitrogen gas cylinder and with heating at  $10^{\circ}$ C min<sup>-1</sup> from 30 to 800 °C. DSC traces were obtained in a differential scanning calorimeter from Mettler Toledo (FP84HT). Heating and cooling rates were 10°Cmin<sup>-1</sup> and ranged from room temperature to 170 °C. Optical textures were captured in a polarized optical microscope from Olympus (BX60) coupled with a temperaturecontrolling hot stage from Mettler (FP82HT) and a digital camera from Hitachi. XRD analysis was performed in a small- and wideangle X-ray scattering instrument from Anton Paar (SAXSess mc<sup>2</sup>) equipped with a sample holder unit (TCS 300-C), an image plate detector, and a temperature control unit (TCU50). Each sample was sealed in a Lindeman glass capillary with an outer diameter of 1.0 mm and a wall thickness of 0.01 mm. The X-rays (Cu\_{K\alpha} radiation;  $\lambda = 0.1542$  nm) were generated at 40 kV and 50 mA. XRD patterns were captured sequentially at determined temperatures on cooling from the isotropic state. The UV/Vis spectra were recorded in a spectrophotometer from Varian (Cary 5000) using a standard quartz cell. The trans-cis photoisomerization was induced in solution (0.05 mg mL<sup>-1</sup> using spectrophotometric grade THF as solvent) by irradiation with a 366 nm nonpolarized handheld UV lamp (UVGL-58). All solutions were irradiated at time intervals up to a PSS.

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**Keywords:** azo compounds • isomerization • liquid crystals • mesophases • phase transitions

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# ARTICLES

Liquid assets: Methacrylic monomers bearing a long azo chromophore core (see picture) show low layer shrinkage at the smectic A to smectic C transition. This unexpected de Vries-like behavior in molecules without highly segregating elements is attractive for applications in optical devices. These monomers also show high *cis*-isomer contents (> 96%) after photoirradiation.



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Azo Monomers Exhibiting Low Layer Shrinkage at the SmA–SmC Transition and *trans–cis* Light-Induced Isomerization