J. Chil. Chem. Soc., 68, N°4 (2023)

Synthesis of a Janus-type structure with liquid crystal properties and photoisomerization study

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ABSTRACT

A new Janus system with liquid crystal properties was synthesized based on units derived from cyanoazobenzene and benzyl ether in its hemispheres, linked by a hydrazide group. The final compound and precursors with liquid crystal properties showed a nematic mesophase. Its mesomorphic properties were studied by polarized light microscopy and DSC. *Cis/trans* isomerization of the azo group in solution and liquid crystal state was studied using UV-Vis spectroscopy.

INTRODUCTION

Searching for new molecular structures with different physical properties is challenging, particularly for technological applications [1]. One of these attractive structures is known as the Janus type structure. Janus structures are special types of molecules whose hemispheres have distinct structural systems, allowing two different types of properties to occur on the same molecule providing asymmetry and can thus impart drastically different chemical or physical properties within a single molecule [2-4]. It was reported that the self-assembly of such structure allows obtaining different properties in the micelle, amphiphilic colloid, optical and liquid crystal fields [3,5-9]. Molecules with such structures could present the ability to self-assembly, leading to materials showing interesting properties in the electronic and biological field [10,11]. One of the most important interests generated by these materials is their multi-functionality and ability to link incompatible systems [12-14].

Since liquid crystal properties are used in numerous applications in electronic devices, the interest in such materials keeps growing, especially in the search for a new structural system that could combine the liquid crystal properties with others [15,16]. An example is dendrimers with liquid crystal properties were reported with interesting properties such as controlled drug releases, nonlinear optics and photoactive materials [17-19]. Furthermore, dendrimers are known for their remarkable ability to self-assembly, could be prepared and orientated to applications according to their functionalities present in the structure [18,20,21].

Incorporating functional groups in a dendritic system generates an interesting synthetic strategy to obtain materials with potential technological applications; for example, the azo group can isomerize in the liquid crystal state or the carbazole group exhibits luminescence depending on the carbazole units [8,19,22,23].

Other fascinating systems with liquid crystal properties are star-shaped, polycatenar, and dendritic structures [24-26]. Recently, a particular interest has been given to materials able to change their physical properties induced by an external factor which could be chemical or physical. Such as the isomerization with light in the stilbenzenes and azobenzene groups, causing a structural and functional transformation in the material [27]. The azo compounds represent a class of molecules, able to change their configuration from trans to cis through a photon induction process in the visible and ultraviolet range [28]. They provide new perspectives in obtaining functional materials that can switch with a specific wavelength. Their incorporation in a molecular structure allows the generation of various structural organizations, especially when combined with materials presenting liquid crystal properties [29]. It is essential to underline that, from this combination, additional relevant properties emerge as optical commutation, dynamic holography, nonlinear optic and high density data storage [30].

Involved in the study of liquid crystals, our investigation group described an organic compound containing a diacylhydra-zine group [31]. This functional group has the characteristic of self-organizing supramolecular by hydrogen bonding around the

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amide groups, providing a liquid crystal state [32,33]. Promoting the gelling properties and stabilizing the mesophase in the liquid crystal state [34-36]. In addition, it is a very attractive functional group as a chelating agent in the preparation of complexes [37].

This paper presents the synthesis of a compound janus type with liquid crystal properties. This *janus* structure contains on one side calamitic mesogenic units functionalized by an azo group, while the other hemisphere contains benzyl ethers, both hemispheres linked by dihydrazide grup. The molecular structures were confirmed by spectroscopic characterization and thermal studies were followed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Mesomorphic studies were discussed using polarized optic microscopy (POM) techniques. In addition, its photophysical properties were studied from the UV-Visible spectrum.

EXPERIMENTAL SECTION

General

All reagents were obtained from commercial sources (Merck or Aldrich) and used without further purification. The organic solvents were of analytical grade quality. The purity of the compounds was checked by thin-layer chromatography (Merck Kieselgel 60F254).

1H NMR and ^{13}C NMR spectra were recorded using a Bruker Ascend 400 MHz spectrometer, with $CDCl_3$ and DMSO-d6 as solvents and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded with a Nicolet Magna 550 spectrometer.
Mesophases analysis was performed using an Olympus BX41 optical microscope equipped with an Olympus U-TV0.5XC-3 polarizer, a Linkam THMS600 heat stage, and an RTVQIMAGING digital camera. Transition temperatures and enthalpies were investigated by DSC using a NETZSCH DSC 204 F1 Phoenix calorimeter. Samples were encapsulated in aluminium pans and observed at scanning rate of 10°C min^{-1} on heating and cooling. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}) under a nitrogen atmosphere.

Ultraviolet absorbance measurements were made with a Shimadzu UV-1800 spectrophotometer, using a 1 cm path cuvette and solution at concentrations of 2.0×10^{-5} mol/L in dichloromethane for UV-Vis study.

Methyl 3,4,5-tris(benzyloxy)benzoate (1):
10.0 g of methyl 3,4,5-trihydroxy benzoate (54.3 mmol), 67.54 g of K_2CO_3 (489 mmol) and 23.46 mL of benzyl bromide (200 mmol) are mixed. The reaction was allowed to stir at room temperature for 5 hours. The mixture is then poured into water and vacuum filtered. The product obtained was recrystallized from an ethanol/water mixture. Yield: 94.5% MP: 103.4°C. FT-IR (KBr) [cm^{-1}]: 2945, 2877 (Csp$_3$–H), 1713 (C=O); 1586 (C=C), 1209 (C-O). 1H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 3.93 (s, 3 H, OCH_3), 5.16 (s, 2 H, OCH_2), 5.18 (s, 4 H, OCH_2), 7.49 - 7.29 (m, 17 H, arom). 13C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 52.3, 71.2, 75.1, 109.1, 125.2, 127.6, 129.0, 128.0, 128.2, 128.5, 128.6, 136.7, 137.5, 142.4, 152.6, 166.7

3,4,5-tris(benzyloxy)benzoic acid (2):
20.08 g of Methyl 3,4,5-tris (benzyloxy) benzoate (44.2 mmol), 8.65 g of KOH (154.7 mmol) are dissolved in 270 mL of a 1: 1 MetOH/H_2O mixture. The reaction was allowed to stir for 48 hours at the reflux temperature (80°C). After the time has elapsed, the mixture is allowed to cool and neutralized with 10% HCl, the solid is vacuum filtered and recrystallized from an ethanol / water mixture.
Yield: 86.3% MP: 203°C. FT-IR (KBr) [cm^{-1}]: 3028 (OH), 2870 (Csp^3–H), 1686 (C=O), 1593 (C=C), 1228 (C-O) ^{1}H RMN (DMSO-d^6, TMS, 400 MHz) δ ppm: 5.03 (s, 2H, OCH_2), 5.17 (s, 4H, OCH_2), 7.24 - 7.47 (m, 17H, arom), 13.0 (s, ^{1}H, OH) ^{13}C RMN (DMSO-d^6, TMS, 100 MHz) δ ppm: 70.7, 74.7, 108.7, 127.9, 128.4, 128.7, 128.90, 137.3, 141.4, 152.5, 167.3

3,4,5-tris(benzyloxy)benzoyl chloride (3):
0.230 g of 3,4,5-tris (benzyloxy) benzoic acid (0.523 mmol) [38], 0.089 mL of oxalyl chloride (1.05 mmol) and 3 drops of DMF as catalyst are mixed, these are dissolved in 20.0 mL of dry dichloromethane. The reaction was allowed to stand at room temperature for 19 hours. Finally, the solvent is evaporated. The compound was used without *prior* purification for the next reaction step.

4-((4-hydroxyphenyl)diazenyl)benzonitrile (4):
6.0 g of 4-aminobenzonitrile (51 mmol) are mixed in 170 mL of water, the mixture is cooled in a water-ice bath between 0-5°C. Then add 4.22 g of $NaNO_2$ (61.2 mmol) dissolved in 15 mL of H_2O, then acidified by adding dropwise 50 mL of a 1: 3 HC^l/H_2O mixture ensuring that the temperature did not exceed 5°C and allowed to stir for 1 hour.

On the other hand, 5.76 g of phenol (61.2 mmol) were dissolved in 40.0 mL of 10% KOH, this solution was poured onto the diazonium salt and allowed to stir for 1 hour, then brought to mild acid pH by adding HCl 10%. Finally, the solid was filtered and recrystallized from an ethanol/H_2O. Yield: 61.3% MP: 204°C. FT-IR (KBr) [cm^{-1}]: 3310 (O–H), 2227 (CN), 1576 (C=C). ^{1}H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 6.94 (m, 2H, arom), 7.82 - 7.98 (m, 6H, arom), 10.54 (s, ^{1}H, OH) ^{13}C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 112.65, 116.61, 123.22, 126.08, 145.72, 154.75, 162.55

4-((4-((8-bromooctyl)oxy)phenyl)diazenyl)benzonitrile (5):
3.5 g of azo compound 4 (15.5 mmol), 5.11 g of triphenylphosphine (19.5 mmol), 3.24 g of 8-Bromo-1-octanol (15.5 mmol) and 3.95g of DIAD (19.5 mmol) are mixed. The reaction is left at room temperature for 96 hours, finally the product was purified by flash colum using dichloromethane as the eluent. MP: 88°C Yield: 78.2%. FT-IR (Disco KBr) [cm^{-1}]: 2930, 2856 (Csp^3–H), 2218 (CN), 1594 (C=C). ^{1}H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 1.41 (m, 8H, CH_2), 1.88 (m, 4H, CH_2), 3.4 (t, 2H, CH_2Br), 4.08 (t, 2H, OCH_2), 7.05 (m, 2H, arom), 7.82 -

7.95 (m, 6H, arom) 13C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 25.9, 28.1, 28. 7, 29.1, 29.2, 32.7, 34.0, 68.4, 113.1, 114.9, 118.7, 123.01, 125.5, 133.2, 146.7, 154.8, 162.8

methyl 3,4,5-tris((8-(4-((E)-(4-cyanophenyl)diazenyl)phenoxy)octyl)oxy)benzoate (6):

6.27 g of 5 (15 mmol), 0.77 g of Methyl 3,4,5-trihydroxy benzoate (4.2 mmol), 3.48 g of K_2CO_3 (25.1 mmol) and 2.09 g of KI (12.6 mmol) were mixed and dissolved in 80 mL of DMF. The reaction was allowed to stir at reflux temperature (80°C) for 48 hours. Subsequently the mixture is cooled and poured into water, finally the solid is vacuum filtered. The product obtained was purified by column chromatography using dichloromethane as the eluent.

Yield: 31.3%. MP: Cr 83°C N141°C. FT-IR (Disco KBr) [cm^{-1}]: 2931, 2856 (Csp_3–H), 2221 (CN), 1715 (C=O), 1591 (C=C), 1250 (C-O). ^{1}H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 1.34 – 1.52 (m, 20H, CH_2), 1.73 – 1.89 (m, 12H, CH_2), 3.92 (S, 3H, OCH_3), 4.00 – 4.10 (m, 12H, OCH_2), 7.01 (m, 6H, arom), 7.29 (s, 2H, arom), 7.80 (m, 6H, arom), 7.93 (m, 12H, arom). ^{13}C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 26.0, 29.3, 52.2, 68.4, 69.1, 73.4, 106.5, 108.0, 114.9, 118.7, 125.5, 133.2, 146.7, 152.8, 154.8, 162.7, 166.9

3,4,5-tris((8-(4-((E)-(4-cyanophenyl)diazenyl)phenoxy)octyl)oxy)benzohydrazide (7):

0.83 g of 6 (0.7 mmol), 10 mL of hydrazine and 20 mL of ethanol were mixed, the reaction was allowed to stir at reflux temperature (80°C) for 48 hours. The mixture is then removed and poured into water, finally the solvent is evaporated and the product is recrystallized from an ethanol/water mixture. MP: Cr 78°C N 130°C Yield: 60.2%.

FT-IR (Disco KBr) [cm^{-1}]: 3308 (NH2), 3056 (N-H), 2929, 2855 (Csp_3–H), 2216 (CN), 1603 (C=O), 1503 (C=C), 1237 (C-O). 1H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 1.85 (m, 12H, CH_2), 4.10 (m, 12H, OCH_2), 1.56 (m, 20H, CH_2), 7.01 (m, 8H, arom), 7.78 (m, 6H, arom), 8.14 (m, 12H, arom). ^{13}C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 26.1, 29.1, 68.2, 69.3, 73.6, 106.8, 107.7, 114.7, 118.3, 125.8, 133.0, 146.5, 152.4, 154.5, 162.8, 165.9

3,4,5-tris(benzyloxy)-N'-(3,4,5-tris((8-(4-((E)-(4-cyanophenyl)diazenyl)phenoxy)octyl)oxy)benzoyl)benzohydrazide (8):

0.24 g of 3,4,5-tris (benzyloxy) benzoyl chloride (0.52 mmol), 0.47 g of 7 (0.40 mmol) and 0.030g of DMAP were mixed, these are dissolved in 50 mL of NMP (dry), then Add 10 drops of triethylamine. The mixture was allowed to stir at room temperature for 41 hours. Subsequently it was poured into water and the pH was adjusted with 10% HCl.

The solid obtained was vacuum filtered and purified by column chromatography using as eluent a dichloromethane/ethyl acetate 3:7 mixture. MP: Cr 86°C N 119°C Iso. Yield: 40.8%. FT-IR (Disco KBr) [cm^{-1}]: 3369 (N-H), 2925, 2855 (Csp_3–H), 2214 (CN), 1594 (C=O), 1501 (C=C), 1246 (C-O). ^{1}H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 1.37 (m, 20H, CH_2), 1.83 (m, 12H, CH_2), 3.94 - 4.10 (m, 12H, OCH_2), 5.09 (m, 6H, OCH_2), 7.02 (m, 2H, arom), 7.28 (m, 6H, arom), 7.79 (m, 6H, arom), 7.93 (m, 12H, arom) ^{13}C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 26.0, 29.3, 68.4, 69.2, 75.2, 105.8, 106.7, 113.2, 114.8, 118.7, 123.1, 125.47, 133.2, 136.5, 146.7, 152.9, 154.8, 162.7

3,4,5-tris((8-(4-((E)-(4-cyanophenyl)diazenyl)phenoxy)octyl)oxy)benzoic acid (9)

1.50 g of Compound 6 was saponified using 0.112 g (2.00 mmol) of KOH in a 100 mL methanol/water (2:1) solution under reflux for 24 h. The solution was cooled, diluted with water and acidified with HC_1. The chiral acid 9 was purified by column chromatography using as eluent ethyl acetate. FT-IR (Disco KBr) [cm^{-1}]: 2928, 2856 (Csp_3–H), 2223 (CN), 1715 (C=O), 1590 (C=C), 1250 (C-O). ^{1}H RMN ($CDCl_3$, TMS, 400 MHz) δ ppm: 1.37 – 1.47 (m, 20H, CH_2), 1.76 – 1.89 (m, 12H, CH_2), 4.05 (m, 12H, OCH_2), 7.0 (m, 6H, arom), 7.3 (s, 2H, arom), 7.8 (m, 6H, arom), 7.93 (m, 12H, arom). ^{13}C RMN ($CDCl_3$, TMS, 100 MHz) δ ppm: 30.7, 33.92, 73.0, 73.6, 77.5, 102.7, 116.3, 118.4, 120.11, 128.017, 130.5, 138.7, 144.6, 147.7, 157.3, 159.0

RESULT Y DISCUSSION

Synthesis

The synthetic route to obtain the janus structure (8) is described in Figure 1 and Figure 2. Figure 1 shows the synthetic route of the hemisphere with the benzyl groups. First, benzylated methyl gallate (1) is obtained with good yields from the alkylation between methyl gallate and benzyl bromide. In the next step, a acid (2) is obtained by basic hydrolysis and subsequent acidification. [38]. This is necessary to obtain the acid chloride (3) using oxalyl chloride, which was used without further purification to synthesize the final compound.

Figure 1. Synthetic route of the hemisphere with the benzyl groups.

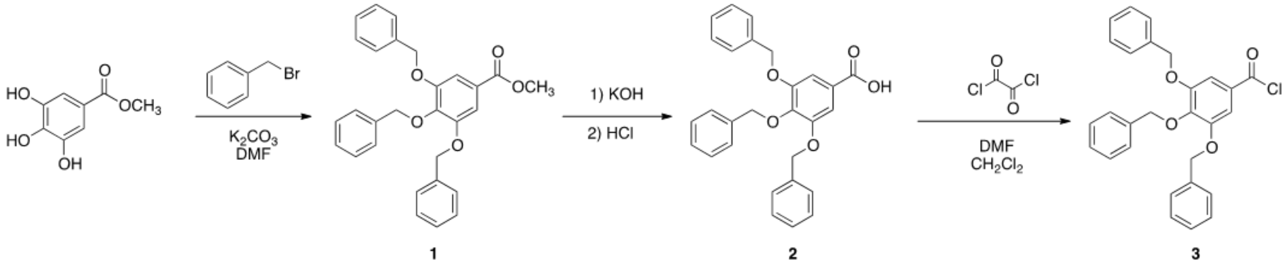


Figure 2. Synthetic route of the hemisphere with the benzyl groups.

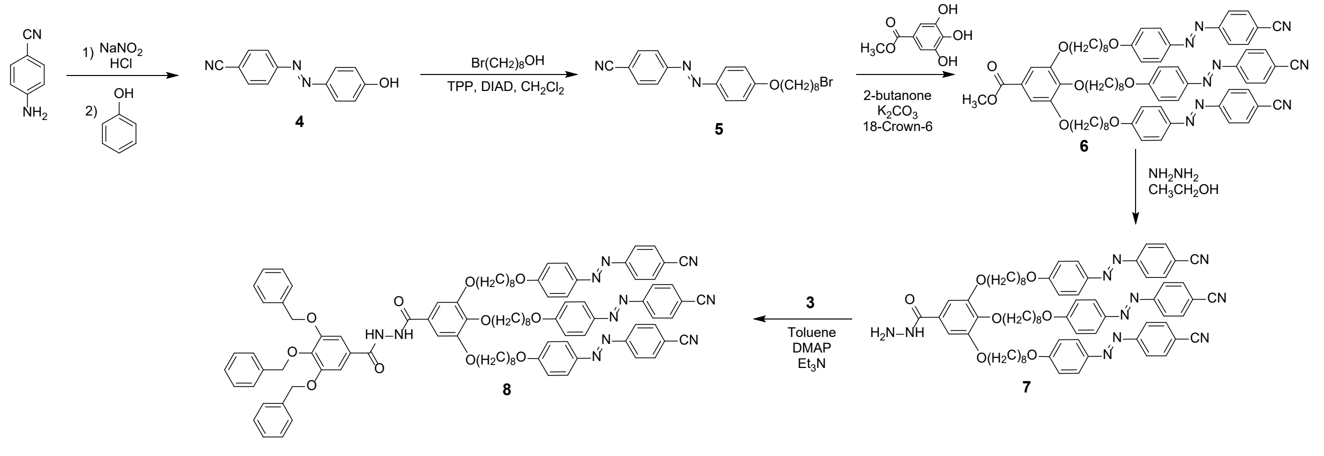


Figure 3. Synthetic route of acid dendron (9).

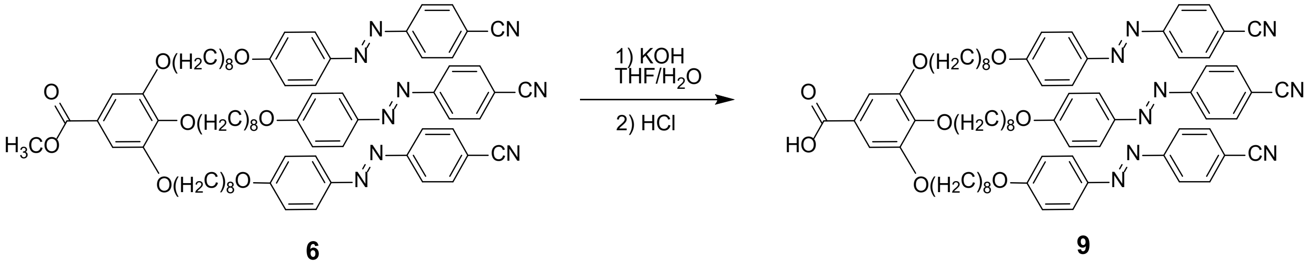


Figure 2 depicts the janus compound (8) synthesis. The azocyanobenzene unit (4) was obtained by reaction with diazonium salt and phenol. The product was alkylated with 8-bromo-1-octanol by Mitsunobu reaction, obtaining excellent yields [39]. The calamitic dendron (6) was synthesized by the Williamson reaction with methyl gallate. Subsequent condensation with hydrazine gives the hydrazide (7). The final compound (8) is obtained using the acid chloride of the benzylated hemisphere (3) and the hydrazide (7).

The synthesized compounds were characterized by FTIR, 13C and ^{1}H NMR. Molecules showing liquid crystal properties were studied by DSC, TGA and MOP.

Compound 8, corresponding to the Janus structure, is obtained as described in Scheme 2. The first step, obtained with good yields, was a reaction between the diazonium salt of 4-aminobenzonitrile and phenol, leading to the formation of the azocianobenzene (4), identified by spectroscopic methods. In the second step, a Mitsunobu reaction on compound 4 using 8-bromo-1-octanol, was carried out, allowing the formation of compound 5 which is obtained with high yields.

The structure of product 5 was evidenced by FTIR analysis showing the disappearance of the OH band and the presence of expected RMN signals, particularly the corresponding to the $-CH_2-O$ group as a triplet at 4.08 ppm. Compound 5 was chemically transformed into product 6 in the third step via a Williamson reaction on methyl gallate. The characterization of compound 6 was successfully established using FTIR and NMR spectroscopy, mainly due to the occurrence of a singlet at 3.92 ppm corresponding to the methyl group.

The next step consisted of a condensation reaction between hydrazine and compound 6, which led to product 7, which was characterized by FT-IR showing the presence of an amine group (3308 and 3056 cm^{-1}). The *janus* product 8 was finally obtained by linking the precursors 7 and 3 through an amide union. The spectroscopy studies confirmed the formation of product 8. Using FTIR analysis, we observed that the double band attributed to $-NH_2$ of compound 7 was converted to a unique band corresponding to –NH- (3369 cm^{-1}) of product 8, showing the amide formation. Moreover, the carbonyl band was slightly shifted to lower values (1594 cm^{-1}). The ^{1}H NMR and ^{13}C NMR spectra of compound 8 present the expected signals with a correct proportion of protons for each signal.

Mesomorphic properties

Polarized light optical microscopy (POM) and differential scanning calorimetry (DSC)were used to investigate the liquid crystal properties of the Janus product and its precursors. The corresponding textures obtained from POM are illustrated in Figure 4; the temperatures of the phase transitions with their enthalpies of transition are indicated in Table 1. Only the precursors 6, 7 and the *janus* (8) product showed mesomorphic behavior. In contrast to compound 5, which did not show liquid crystal properties, the mesophase behavior of compound 6 is probably due to a lack of mobility of azocyanobenzene units. Which promotes and induces ordered molecular organization.

Table 1. Phase-transition temperatures (°C) and associated enthalpy change for the products exhibiting liquid crystals properties. Cr, crystal; N, nematic mesophase; Tg, glass transition; I, isotropic phase.

Compounds	Transition temperature (°C) and ΔH [J/g]	ΔT(°C)
6	Tg 68* N (19.2) 130 I I 128 (1.5) N 60*Tg	62
7	Tg 83 * N 145* I I 141 * N 75 * Tg	58
8	Tg 89 * N 119* I I 119 * N 86* Tg	31
9	Tg 70 * N 135 (1.8) I I 135 (1.8) N 75 * Tg	65

*P** Optical microscopy data

Com-pound 6 exhibits a wide mesomorphic range of 62°C and a nematic phase. However, a DSC analysis of this compound showed the presence of a glass temperature (68°C), the mesophase-solid transition could not be observed in the cooling process. The chemical transformations of the precursors 6 to produce the compound 7 and the final Janus product 8 did not result in a change in the mesophase; the nematic mesophase is preserved in these compounds. Compounds 7 and 8's clearing temperatures were determined. (Table 1)

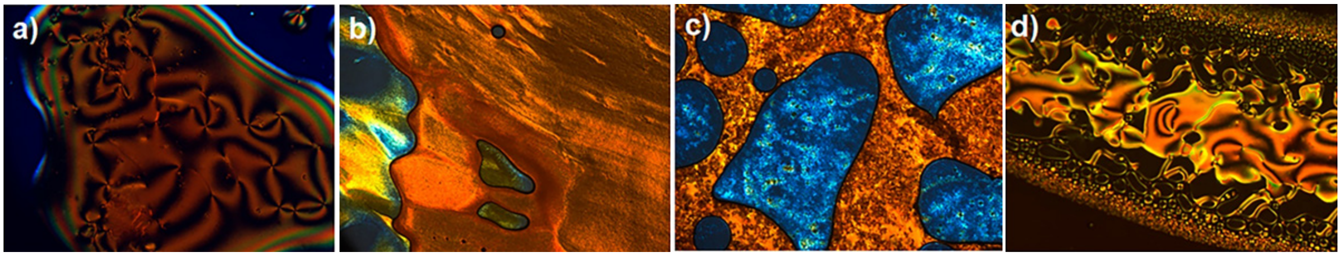
The highest clearing temperature, corresponding to compound 7, explains the wide range of liquid crystal stability. However, the strong intermolecular interaction due to hydrogen bonds in this molecule induces a solidification at higher temperature maintaining the Tg. Compound 8 showed lower clearing and crystallization temperature, due to the benzyl groups which disturb the supramolecular organization Other studies on Janus dendritic systems with benzyl groups in one of their hemispheres have yielded different results depending on the structural characteristic of the opposite hemisphere [10,11].
Parra *et al.,*[31] reported diacylhydrazines with calamitic structures, showing a lamellar-type arrangement (SmC). This and other works by XRD study evidenced that the stabilization of the mesophase is attributed to the interaction by hydrogen bonding of the hydrazine groups with their neighboring molecules[32,40-42].

However, compound 8 has an evident steric hindrance that obstruct efficient hydrogen bonding interaction of hydrazine groups. This allows for the appearance of a one-dimensional organization (nematic mesophase) rather than a two-dimensional organization (smectic mesophase). Even with a hemisphere does not promote good organization, the Janus compound still has liquid crystal properties.

While the transition energies from the isotropic state to the nematic mesophase (N) are very small and for compounds with a high molar mass, it is normal that a peak is not observed in the DSC. The glass transition (Tg) is a second order transition and it is expected that energy associated with DSC does not appear. Due to the complement of the DSC and MOP techniques, the transition temperatures can be obtained.
To obtain another type of organization, such as lamellar or columnar mesophase, the methyl ester group of compound 6 was chemically transformed in acid to obtain compound 9 (Figure 3). The acid group can form a dimer structure through a hydrogen bond. However, this behavior change did not succeed, keeping a nematic type of organization.

The mesophase exhibited by 6, 7, 8 and 9 compounds were identified from the optical texture observed by polarizing optical microscopy (POM) using the classification systems reported by Sackmann and Demus [43] and Gray and Goodby [44]. Figure 1 shows the textures of the compounds 6, 7, 8 and 9 observed in

Figure 4. Optical textures (10x) observed under POM for the compounds: (a) compound 6 at 83°C, 200x, (b) compound 7 at 97°C, 100x, (c) compound 8 at 108°C, 200x, (d) compound 9 a 106°C, 200x. All photomicrographs were taken during the cooling process from the isotropic liquid.



*P** Optical microscopy data

Table 2. UV-visible absorption data for compounds 6, 8 and 9.

Compound	Absorption*λabs-max [nm]	Absorbance*	Log ε
6	364.6	0.133	4.82
8	365.4	0.129	4.80
9	365.7	0,036	4.25

*:Determined in dichloromethane solution 2.00×10^{-5} [mol L^{-1}].

the liquid crystal state from the polarized optical microscopy. Nematic mesophases were observed presenting schlieren (Figure 4A and Figure 4D) and marble (Figure 4B and Figure 4C) textures.

Ultraviolet visible absorption

Compounds 6, 7, 8 and 9 were studied by UV-Vis spectroscopy in dichloromethane solutions with concentrations of 2.0×10^{-5} mol L^{-1}; all of the compounds exhibit the same behavior (Figure 5), with maximum absorption at 365 nm associated with the azo group's π-π* transitions corresponding to the *trans* isomer, which is the thermodynamically more stable conformation [28].

Table 2 summarizes the most important data from Figure 2 as well as the molar absorptivity value for each liquid crystal compound, calculated using Lambert-Beer's law.

Isomerization

An isomerization study of compound 8 was carried out in dichloromethane (1.0×10^{-3} mol L^{-1}). The solution was irradiated with a UV commercial lamp with a wavelength of 365 nm (Philips PL-S 9 W) at one minute intervals.

The graph is represented in Figure 6 and shows the decrease in the 365 nm band at two isosbestic points (364 and 424 nm) corresponding to the π-π* transition of the trans conformation and a band appearing at 450 nm corresponding to the n-π* transition of the cis conformation [45,46]. After one minute of irradiation, the sample showed partial isomerization and after two minutes the sample reached a stationary state with one absorbance maximum appearing at 450 nm, supporting the presence of the cis isomer. The new absorption maximum at 450 nm corresponds to the n-π* transition.

The process is reversible; when irradiated with visible light (450 nm) there is an increase and decrease in intensities of the bands associated with the trans and cis isomers, respectively. Compound 8 was irradiated in mesophase to study the behavior of the liquid crystal state in *cis/trans* isomerization; in previous works, it has been observed that these materials lose this property when irradiated [47].

In the case of this material, when irradiated by different power and at different times, in the order of minutes, no significant change is observed, maintaining the mesophase (Figure 7). This is relevant since the mesophase of this material is relatively stable even if the conformation of the azo group changes from *trans* to cis due to the effect of photoisomerization.

Mixture

In dichloromethane, an equimolar proportion of the benzylated hemisphere (1) and the one with azo units (6) was prepared. The solution was left stirring until all the solvent had evaporated.

The resulting mixture was observed under the POM (Figure 8) and its behavior showed a segregation of phases, a liquid crystal

Figure 5. Absorption spectrum of compounds 6, 8 and 9 in dichloromethane 2.00×10^{-5} mol L^{-1}.

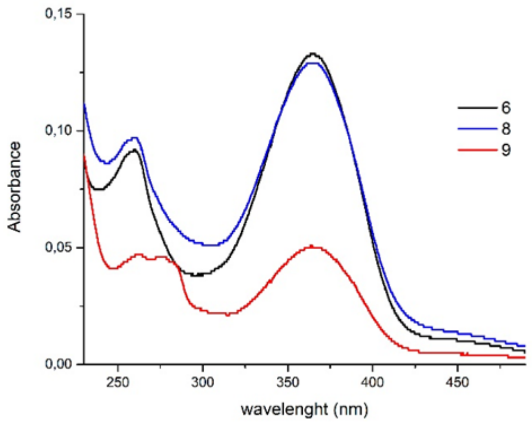


Figure 6. UV-Vis absorption spectrum for compound 8 when irradiated with 365 nm UV light.

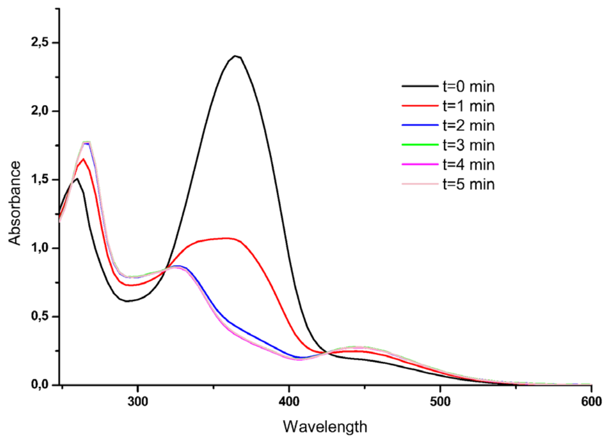


Figure 7. Compound 8 in liquid crystal state observed by POM, the sample was exposed to different irradiation times with a 365 nm UV lamp.

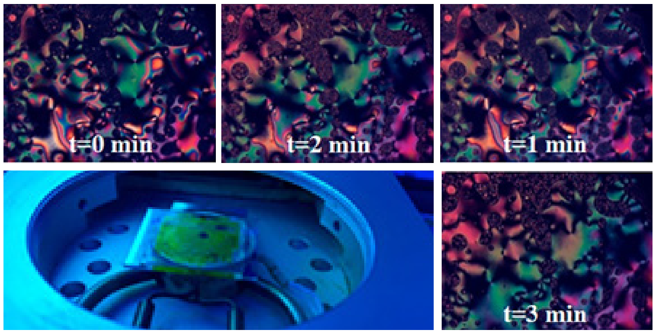
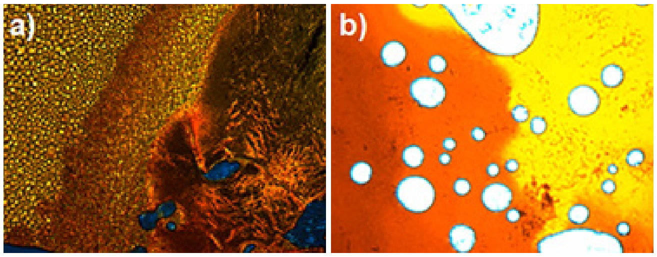


Figure 8. Microphotographs of the physics mixture between compounds 1 and 6. (a) with crossed polarizers; (b) no crossed polarizers.



phase and a solid phase. The segregation of the two units explains an incompatibility between the two hemispheres. The only way to have a homogeneous interaction is the chemical union of both hemispheres, such as compound 8.

CONCLUSION

A new *janus* dendritic system connected by a diacylhydrazine group with liquid crystal and photoisomerizable properties was obtained. The structural organization of a material (*cis/trans*) is altered when it is irradiated with a specific wavelength. Adding three azo groups per molecule does not prevent the material from losing its liquid crystal properties when irradiated. This is an interesting result for developing photochemical sensors.

ACKNOWLEDGMENTS

This research was supported by FONDECYT [grant number 1140350].

REFERENCES

1. M. Javadzadeh, J. del Barrio, C. Sanchez-Somolinos. *Adv. Mater.* 35, (2023).
2. P. H. J. Kouwer,G. H. Mehl, J. Mater. Chem. 19, 1564, (2009).
3. A.-M. Caminade, R. Laurent, B. Delavaux-Nicot, J.-P. Majoral. *New J. Chem.* 36, 217, (2012).
4. I. M. Saez, J. W. Goodby. *Chem. Eur.* J. 9, 4869, (2003).
5. T. M. N. Trinh, T. T. Nguyen, C. Kopp, P. Pieper, V. Russo, B. Heinrich, B. Donnio, T. L. A. Nguyen,R. Deschenaux. *Eur. J. Org. Chem.* 2015, 6005, (2015).
6. N. Gimeno, J. Vergara, M. Cano, J. Luis Serrano, M. Blanca Ros, J. Ortega, C. L. Folcia, S. Rodriguez-Conde, G. Sanz-Enguita, J. Etxebarria. *Chem. Mater.* 25, 286, (2013).
7. J. Vergara, N. Gimeno, M. Cano, J. Barberá, P. Romero, J. L. Serrano, M. B. Ros. *Chem. Mater.* 23, 4931, (2011).
8. E. Fedeli, A. Lancelot, J. Luis Serrano, P. Calvo, T. Sierra, *New J. Chem*. 39, 1960, (2015).
9. W. Chen, H.-J. Sun,T. Miyoshi, *J. Phys. Chem. B.* 117, 13698, (2013).
10. V. Percec, M. R. Imam, T. K. Bera. V. S. K. Balagurusamy, M. Peterca, P. A. Heiney, Angew. Chem., *Int. Ed.* 44, 4739, (2005).
11. V. Percec, D. A. Wilson, P. Leowanawat, C. J. Wilson, A. D. Hughes, M. S. Kaucher, D. A. Hammer, D. H. Levine, A. J. Kim, F. S. Bates, K. P. Davis, T. P. Lodge, M. L. Klein, R. H. DeVane, E. Aqad, B. M. Rosen, A. O. Argintaru, M. J. Sienkowska, K. Rissanen, S. Nummelin, J. Ropponen, *Science.* 328, 1009, (2010).
12. P. H. J. Kouwer, G. H. Mehl, *J. Am. Chem. Soc.* 125, 11172, (2003).
13. P. H. J. Kouwer, S. J. Picken, G. H. Mehl, J. *Mater. Chem.* 17, 4196, (2007).
14. I. M. Saez, J. W. Goodby, *Chem. Commun.* 17, 26, (2003).
15. I. M. Saez, J. W. Goodby, *J. Mater. Chem.* 15, 26, (2005).
16. C. Tschierske, *Chem. Soc. Rev.* 36, 1930, (2007).
17. J. Barbera, B. Donnio, L. Gehringer, D. Guillon, M. Marcos, A. Omenat, J. L. Serrano. *J. Mater. Chem.* 15, 4093, (2005).
18. B. Donnio, S. Buathong, I. Bury, D. Guillon. *Chem. Soc. Rev.* 36, 1495, (2007).
19. N. Gimeno, J. Vergara, M. Cano, J. L. Serrano, M. B. Ros, J. Ortega, C. L. Folcia, S. Rodriguez-Conde, G. Sanz-Enguita, J. Etxebarria, *Chem. Mater.* 25, 286, (2013).
20. A. K. Srivastava, D.-Y. Kim, J. Kim, J. Jeong, J.-H. Lee, K.-U. Jeong, V. Singh. *Liq. Cryst.* 43, 920, (2016).
21. I. Gracia, B. Feringan, J. L. Serrano, R. Termine, A. Golemme, A. Omenat, J. Barbera, *Chem. Eur. J.* 21, 1359, (2015).
22. S. Castelar, P. Romero, J.-L. Serrano, J. Barberá, M. Marcos. *RSC Adv.* 5, 65932, (2015).
23. I. Gracia, B. Feringán, J. L. Serrano, R. Termine, A. Golemme, A. Omenat, J. Barberá. *Chem. Eur. J.* 21, 1359, (2015).
24. F. A. Olate, M. L. Parra, J. M. Vergara, J. Barberá, M. Dahrouch. *Liq. Cryst.* 44, 1173, (2017).
25. F. A. Olate, J. A. Ulloa, J. M. Vergara, S. A. Sanchez, J. Barbera, M. L. Parra. *Liq. Cryst.* 43, 811, (2016).
26. E. Y. Elgueta, M. L. Parra, J. Barberá, J. M. Vergara, M. Dahrouch, E. W. Díaz. *Liq. Cryst.* 43, 1649, (2016).

27. A. S. Lubbe, W. Szymanski, B. L. Feringa. *Chem. Soc. Rev.* 46, 1052, (2017).
28. H. M. D. Bandara, S. C. Burdette. *Chem. Soc. Rev.* 41, 1809, (2012).
29. N. A. Razali,Z. Jamain. *Polymers.* 13, 3462, (2021).
30. J. del Barrio, C. Sánchez-Somolinos. *Adv. Opt. Mater.* 7, 1900598, (2019).
31. M. Parra, P. Hidalgo, J. Barbera, E. Carrasco,C. Saavedra. *Liq. Cryst.* 33, 391, (2006).
32. Y. Wu, C. Zhang, Y. Zhang, B. Bai, H. Wang, M. Li. *Liq. Cryst.* 41, 1854, (2014).
33. D. Pang, H. Wang,M. Li. *Tetrahedron.* 61, 6108, (2005).
34. B. Bai, H. Wang, H. Xin, J. Shi, B. Long, M. Li. *J. Phys. Org. Chem.* 20, 589, (2007).
35. H. Wang, R. Shao, C. Zhu, B. Bai, C. Gong, P. Zhang, F. Li, M. Li,N. A. Clark. *Liq. Cryst.* 35, 967, (2008).
36. B. Bai, H. Wang, H. Xin, F. Zhang, B. Long, X. Zhang, S. Qu, M. Li. *New J. Chem.* 31, 401, (2007).
37. B. T. Heaton, C. Jacob, P. Page, *Coord. Chem. Rev.* 154, 193, (1996).
38. M. Das, K. Senapati, S. S. Panda, P. Bhattacharya, S. Jana, S. M. Mandal, A. Basak. *RSC Adv.* 6, 85254, (2016).
39. K. C. K. Swamy, N. N. B. Kumar, E. Balaraman, K. V. P. P. Kumar. *Chem. Rev.* 109, 2551, (2009).
40. S. Qu, F. Li, H. Wang, B. Bai, C. Xu, L. Zhao, B. Long, M. Li. *Chem. Mater.* 19, 4839, (2007).
41. P. Zhang, S. Qu, B. Bai, H. Wang, X. Ran, C. Zhao, M. Li. *Liq. Cryst.* 36, 817, (2009).
42. P. Zhang, H. Wang, H. Liu, M. Li, Langmuir. 26, 10183, (2010)
43. H. Sackmann, D. Demus. *Mol. Cryst.* 2, 81, (1966)
44. G. G. G. JWG. *Smectic Liquid Crystals: Textures and Structures.* XVI ed. G. Leonard Hill. Leonard Hill, Glasgow, 1984.
45. D. Y. Kim, S. A. Lee, Y. J. Choi, S. H. Hwang, S. W. Kuo, C. Nah, M. H. Lee, K. U. Jeong, *Chem. Eur. J.* 20, 5689, (2014).
46. C. Selvarasu, P. Kannan, *J. Mol. Struct.* 1092, 176, (2015).
47. D. Y. Kim, S. A. Lee, H. Kim, S. M. Kim, N. Kim,K. U. Jeong, *Chem. Commun.* 51, 11080, (2015).