



## Design of New V Shaped Thermotropic Liquid Crystals containing Heterocyclic

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### Abstract

The characterization and design of this study of new liquid crystals with were reported. This study reported the characterization and design of new liquid crystals with a V shape compounds containing thiazolidine-2,4-dione and 1,3-phenylene as a core unite with mesophase properties. Chloroacetic acid, water, and thiourea were used to prepare thiazolidine-2,4-dione [I] in the presence of strong hydrochloric acid. The 4-hydroxybenzaldehyde and n-alkyl bromide were reacted with potassium hydroxide to create the n-alkoxy benzaldehyde, and then the compound [I] reacted with [II]<sub>n</sub> in the presence of piperidine to produce compounds [III]<sub>n</sub>. In addition, resorcinol was converted to a corresponding compound [IV] by refluxing pyridine and DMF with two moles of chloroacetyl chloride; the compounds [III]<sub>n</sub> and [IV] were then interacted with sodium acetate to form compounds [V]<sub>n</sub>. FT-IR and <sup>1</sup>HNMR spectroscopy were really used to determine the structures of the produced substances. Using polarized optical microscopy, these mesogens' mesomorphic characteristics were studied (POM). The synthesized molecules exhibited enantiotropic liquid crystal phases; the substances [V]<sub>1-4</sub> exhibited an only the enantiotropic nematic phase.

**Keywords:** thiazolidine-2,4-dione, heterocyclic, thermotropic LC, V liquid crystals.

### 1. Introduction

Heterocyclic compounds are an important class of organic compounds with many applications in various fields of science [1]. Five-membered heterocyclic compounds with liquid crystalline properties have been successfully evaluated [2,3]. In general, the molecule is made up of connecting units, terminal groups, and long, flexible chains with flat, stiff cores [4]. Mesogenic molecules' ability to arrange themselves and self-assemble is influenced by molecular shape. In

order to create a mesogenic molecule, it is crucial to select the right core, connecting unit, or terminal group.

In the course of researching heterocyclic liquid crystal derivatives, various thermotropic liquid crystals with heterocyclic units have been created over a long period of time. [5,6] In line with our investigation of heterocyclic unit-containing derivatives of liquid crystals, various thermotropic liquid crystals with heterocyclic units have been created over a long period of time. [7-9]. The geometry of rigid-cored calamitic molecules has been thought to be the most conducive to mesogenic activity. [10]. Therefore, understanding the link between structure and property is crucial when developing new liquid crystal materials.

Numerous mesogens have been created and studied as a result of the utilization of novel thermotropic liquid crystals [11]. Examples of real-world LC applications in science and technology include display devices, photoconductors, organic light-emitting diodes, and semiconductor materials. [12-14].

In this paper, we synthesize a new V homologous series bearing two arms containing thiazolidine-2,4-dione with an alkoxy chain and study their liquid crystal properties. There are no known substances with properties and synthesis identical to those of liquid crystals. Based on the various alkoxy chains' lengths, the liquid crystalline compounds' characteristics were explained. Understanding the impact of these molecules' skeletal structures and their capacity to induce the liquid crystal mesophase is the primary goal of this work.

## 2. Experimental

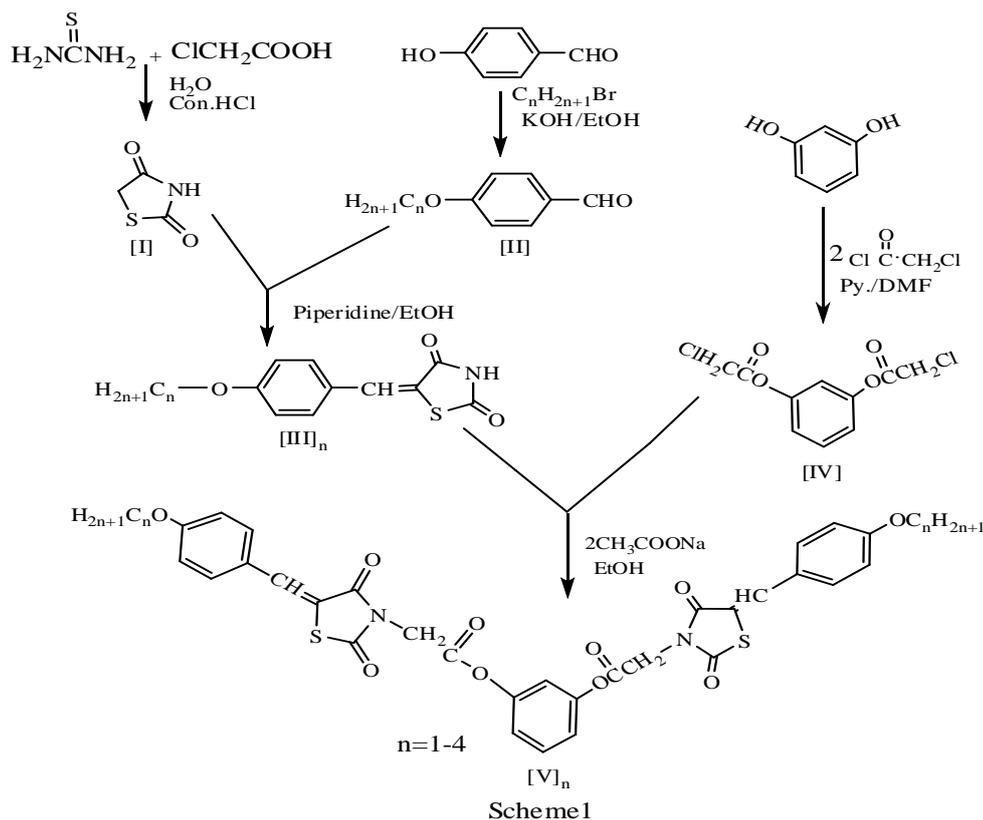
Materials were obtained from Merck Co., Fluka, and Aldrich.

### Techniques

With the TMS serving as an internal standard, the compounds were dissolved in DMSO-d<sub>6</sub> solution; the <sup>1</sup>H-NMR Spectra were measured at 400 MHz by the company Bruker and reported in ppm (δ). SHIMADZU recorded FT-IR spectra (IR Affinity<sup>1</sup>) in the 400–600 cm<sup>-1</sup> wavenumber range of the FT-IR spectrometer. The method was used by Gallen Kamp to test melting point. An INSTEC Hot stage and a Meiji MT9000 Polarizing Optical Microscope were used to examine the properties of liquid crystals.

### Synthesis

Scheme 1 shows the pathway of the newly produced compounds:

Scheme 1: route synthesis of compounds [I-V<sub>4</sub>]

## Synthetic procedures

### Preparation of the Thiazolidine-2,4-dione [I]

A flask of 250 ml with three necks was filled with a mixture of 45.6g (0.6M) of thiourea and 56.4g (0.6M) of chloroacetic acid. The mixture was left until the appearance of white precipitate then it was agitated for 15 minutes at 100–110 °C, the reaction mixture was agitated and refluxed for 10–12 hours. At this point, 60 ml of concentrated hydrochloric acid was carefully added using a falling funnel to dissolve the precipitate. The mixture of reactions solidified into a mass of white needle clusters after cooling to get rid of any remaining hydrochloric acid. The filtered item was washed with water, dried, and then recrystallized from ethanol, yielding 80%, M.P 123–125 °C [15].

FTIR( $\text{cm}^{-1}$ ): 3135 (v N-H), 3047 (v arom.-H), 2947-2823 (v aliph.-H), 1735 to 1654 (vC=O), 617(C-S).

### General Procedure of Prepared 4-n-alkoxybenzaldehyde[II]<sub>n</sub>

4-hydroxybenzaldehyde (10.61 g, 0.087 mole) and 0.13 mole of n-alkyl bromide, absolute ethanol (50 mL), potassium hydroxide (4.87g, 0.087 mol), diethyl ether (50 mL) with water (50 mL) were all added to a (4.87g, 0.087 mole) of potassium hydroxide solution in 100 ml ethanol. The mixture was then refluxed, using 25 mL of water and 10% sodium hydroxide in 25 mL. 25 mL of water was added after the mixture's synthetic phase had been removed. To get oily 4-alkoxybenzaldehyde, the organic layer was separated and dried over anhydrous magnesium sulfate, then filtered and evaporated [16], yielding (75-80%).

**Synthesis of 5-Arylidene-thiazolidine-2,4-dione: General Procedure [III]<sub>n</sub>**

A mixture of compound [I] (2.21g, 0.01mole) and aromatic aldehyde[II]<sub>n</sub> (0.01mole) with 5mL ethanol was refluxed for three hours while piperidine (0.5mL) was present. The product was then cooled before being placed in cold water. The solid was cleaned, dried, and recrystallized from acetone after filtering and cleaning.

**5-(4-methoxybenzylidene) thiazolidine-2,4-dione[III]<sub>1</sub>**

Molecular formula C<sub>11</sub>H<sub>9</sub>NO<sub>3</sub>S, Yield 95%, M.P 219Lit[15]216-218° C, Color light yellow  
FTIR(cm<sup>-1</sup>): 3224 (ν N-H), 3016(ν (C-H arom.)), 2958-2835(νC-H aliph.), 1732-1693(νC=O thiazolidinone), 1589(νC=C), 1257(νC-O).

**5-(4-ethoxybenzylidene)thiazolidine-2,4-dione[III]<sub>2</sub>**

Molecular formula C<sub>12</sub>H<sub>11</sub>NO<sub>3</sub>S, Yield 85%, M.P 189° C, Color light brown  
FTIR(cm<sup>-1</sup>): 3240(ν N-H), 3074(ν (C-H arom.)), 2981-2827(ν C-H aliph.), 1735-1697 (νC=O thiazolidinone), 1600 (νC=C), 1257(νC-O).

**5-(4-propoxybenzylidene)thiazolidine-2,4-dione[III]<sub>3</sub>**

Molecular formula C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>S, Yield 78%, M.P 207° C, Color yellow  
FTIR(cm<sup>-1</sup>): 3406(ν N-H), 3062(ν (C-H arom.)), 2939-2808 (ν C-H aliph.), 1743-1697 (νC=O thiazolidinone), 1612(νC=C), 1253(νC-O).

**5-(4-butoxybenzylidene)thiazolidine-2,4-dione[III]<sub>4</sub>**

Molecular formula C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>S, Yield 75%, M.P 174° C, Color dark brown  
FTIR(cm<sup>-1</sup>): 3406(ν N-H), 3059(ν (C-H arom.)), 2997-2839(ν C-H aliph.), 1743-1685(νC=O thiazolidinone), 1597(νC=C), 1280(νC-O).

**Preparation of 1, 3-phenylene bis(2-chloroacetate) [IV][17]**

Chlororo acetylchloride (0.002mole) was slowly added to a stirred solution of resorcinol (0.11g,0.001mole), pyridine 1mL, and DMF 2mL at 48 °C. Then, 10% HCl was added to the reaction mixture, which had been stirred for three hours at ambient temperature. The precipitate was subsequently filtered, washed with water and dried. The ethanol residue was recrystallized.  
Molecular formula C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub> ,: reddish color,yield70%,m.p.=66-68°C

**Synthesis of 1,3-phenylene bis(2-(5-(4-alkoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) [V]<sub>n</sub>**

Reluxing was done for four hours with a mixture of compounds [III]<sub>n</sub> (0.002mole), compound [IV] (0.001mole), sodium acetate (0.16g, 0.002mole), and ethanol (5mL). Ice water was then added when the mixture had been cooled. After filtering, the mixture was acidified with 10% HCL. After adding ethyl acetate to get chemicals, the organic layer was separated and dried.

**1,3-phenylene bis(2-(5-(4-methoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) [V]<sub>1</sub>**

Molecular formula C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, Yield 95 %, M.P 76°C, Color off white  
FTIR(cm<sup>-1</sup>): 3093 (ν C-H arom.), 2927-2854 (ν C-H aliph.), 1732-1693 (ν C=O), 1589 (νC=C), 1288 (νC-O), 1149 (νC-N).

**1,3-phenylene bis(2-(5-(4-ethoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate)[V]<sub>2</sub>**

Molecular formula C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, Yield80 %, M.P 110°C, Color yellow  
FTIR(cm<sup>-1</sup>): 3097 (ν C-H arom.), 2993-2962 (ν C-H aliph.), 1724-1681 (ν C=O), 1593 (νC=C), 1280 (νC-O), 1149 (νC-N).

**1,3-phenylene bis(2-(5-(4-propyloxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate)[V]<sub>3</sub>**

Molecular formula C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, Yield75 %, gumme, Color brown  
FTIR(cm<sup>-1</sup>): 3024 (ν C-H arom.), 2970-2839 (ν C-H aliph.), 1735-1693 (ν C=O), 1604 (νC=C), 1284 (νC-O), 1149 (νC-N).

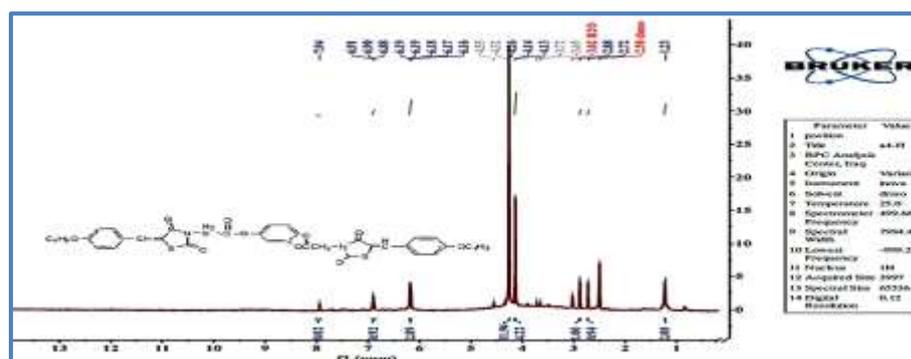
**1,3-phenylene bis(2-(5-(4-butoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate)[V]<sub>4</sub>**Molecular formula C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, Yield 80 %, gumme, Color brownFTIR (cm<sup>-1</sup>): 3012 (ν C-H arom.), 2954-2840 (ν C-H aliph.), 1735-1697 (ν C=O), 1604 (ν C=C), 1211 (ν C-O), 1149 (ν C-N).<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): (7.94-6.16) (m, 12H, Ar-H & 2H, 2CH=C), (4.26-4.14) (t, 4H, 2OCH<sub>2</sub>), (2.72-3.72) (m, 4H, 2 CH<sub>2</sub>N & 8H, 2 (CH<sub>2</sub>)<sub>2</sub>), 1.23 (t, 6H, 2 CH<sub>3</sub>).**3. Results and Discussion**

Equimolar amounts of thiourea and chloroacetic acid were reacted to produce 2,4-thiazolidinedione [I]. The derivatives [II]<sub>n</sub> were then synthesized by reacting absolute ethanol with 4-hydroxybenzaldehyde, which was then combined with alkylbromide and potassium hydroxide. Knoevenagel used condensation to create compounds [III] by combining selected aromatic aldehydes with compound [I]. These compounds infrared spectra revealed a prominent functional group absorption band that ranged between 1589 and 1612 cm<sup>-1</sup> for C=C and 1743, 1685 cm<sup>-1</sup> for the carbonyl groups at the thiazolidine-2,4-dione ring at positions 2 and 4 [18].

We combined resorcinol with two moles of chloroacetyl chloride in pyridine and DMF to create the derivative [IV]. The FTIR spectrum of compound [IV] revealed a disappearing band for the OH group that was present in the starting material as well as at 1732 cm<sup>-1</sup>; a new absorption extending band<sup>-1</sup> that was attributed to the ester group's C=O. A stretching band for CH<sub>2</sub>Cl was also shown at 790 cm<sup>-1</sup>.

From the reactions of two moles of compounds [III]<sub>n</sub> and one mole of compounds [IV] with sodium acetate in ethanol, we obtained the compounds [V]<sub>n</sub>. The absorbance bands of N-H and CH<sub>2</sub>-Cl for the starting materials vanished from these substances' FTIR spectra, while new bands of the C-N and C=O ester groups appeared at 1149 cm<sup>-1</sup> and 1735–1681 cm<sup>-1</sup>, respectively.

**Figure 1** represents the <sup>1</sup>H-NMR spectrum for compound [VI]<sub>4</sub>. DMSO was used as a solvent. The following distinctive chemical changes were noticed: multiplet indications of two CH=C group protons and twelve aromatic protons at (6.16-7.94) ppm, a triplet signal at δ(4.26-4.14) ppm for four protons of OCH<sub>2</sub> groups, and also multiplet signal at (2.72-3.72) ppm for four protons of CH<sub>2</sub>N and eight protons of two (CH<sub>2</sub>)<sub>2</sub> groups and a triplet signal at 1.23 ppm.



**Figure 1:** The <sup>1</sup>H-NMR spectrum for compound [V]<sub>4</sub>

**Liquid Crystalline Properties**

The properties of liquid crystalline compounds were assessed using polarized optical microscopy [V]<sub>n</sub> (POM). Under polarized light and at a specific temperature, POM exhibits liquid crystal characteristics.

The values for the transition temperatures were shown in **Table 1**. Microscopy examinations were used to determine the mesophase's texture using the Richter [19] and Gray and Goodby categorization systems. [20].

**Table 1:** The temperatures at which compounds in the series [V]<sub>n</sub> change into phase

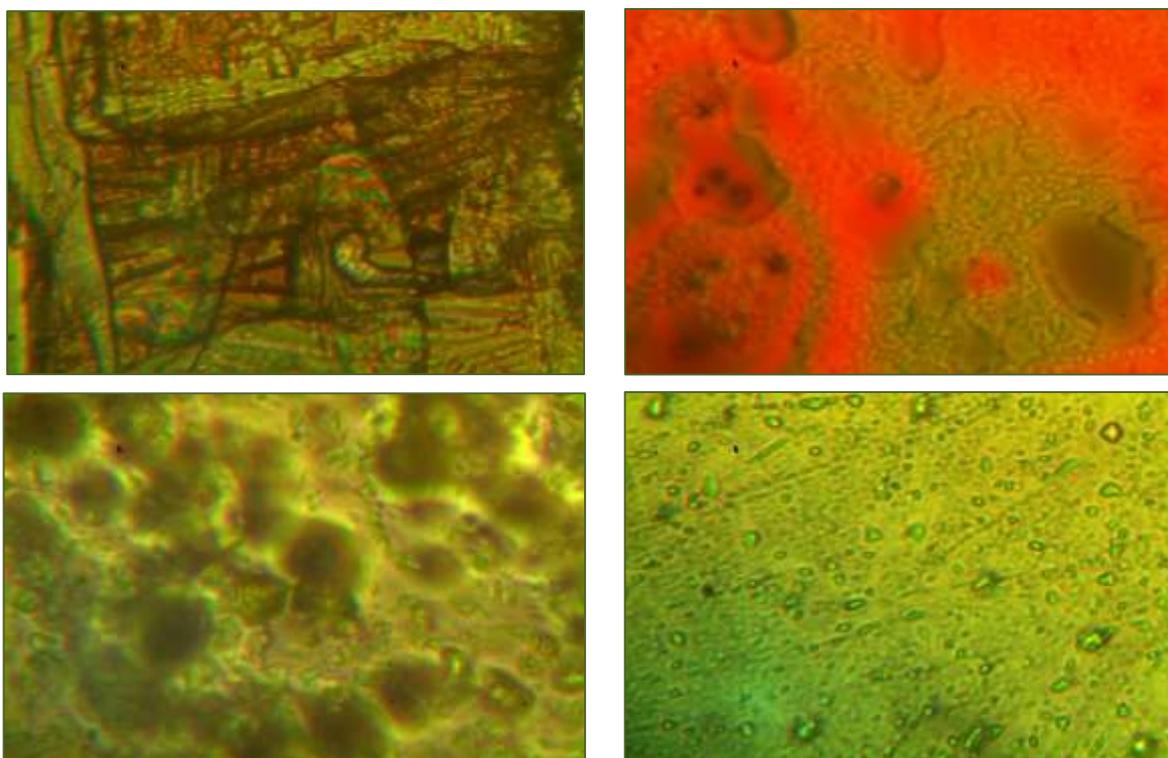
Compound	Phase transition
[V] <sub>1</sub>	Cr $\xrightleftharpoons{195}$ N $\xrightleftharpoons{230}$ I
[V] <sub>2</sub>	Cr $\xrightleftharpoons{210}$ N $\xrightleftharpoons{300}$ I
[V] <sub>3</sub>	Cr $\xrightleftharpoons{160}$ N $\xrightleftharpoons{250}$ I
[V] <sub>4</sub>	Cr $\xrightleftharpoons{180}$ N $\xrightleftharpoons{270}$ I

Cr , Crystalline Phases ; Isotropic Liquid and Nematic Phase, respectively

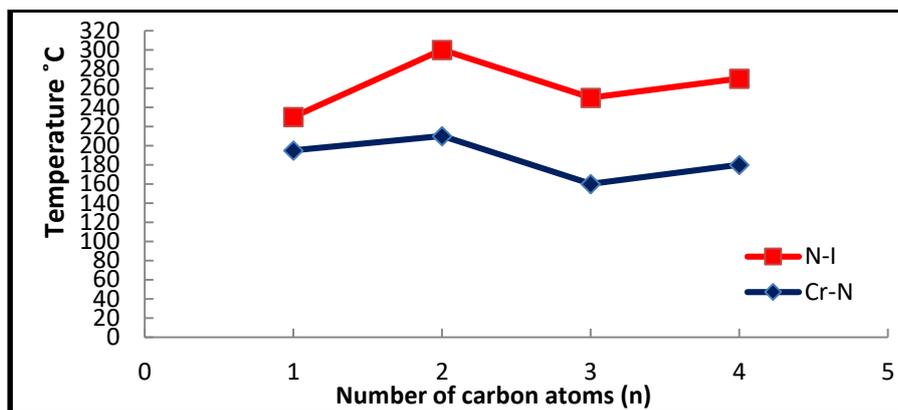
Novel symmetrical compounds bearing two arms containing Thiazolidine-2,4-dione with connected to the core by 1,3-phenylene were successfully synthesized via many-steps. Thus, it can be inferred that in order to manage the phase-transition properties of LC compounds, it is crucial to consider both the molecular geometry and the length of the flexible alkoxy unit.

Only under POM is there an enantiotropic nematic phase in the compounds [V]1-4, as seen by the texturing of the nematic phase in figures (2a–d), respectively. The alkoxy chain of series [V]<sub>n</sub>'s transition temperature is plotted. Consider Figure 3's n, which represents the number of carbon atoms.

This behavior can be characterized in terms of the terminal/lateral (t/l) contact forces ratio, resulting from the size of the alkoxy terminal chain. When this ratio is high, chemicals produce fewer organized mesophases (nematic mesophase), and when it is low, compounds produce more ordered mesophases (smectic phase).



**Figure 2:** polarization-reversing optical textures (a) compound [V]<sub>1</sub>'s phase obtained in the nematic phase for compound [V] after cooling at 200 °C. (b) compound [V]<sub>2</sub> heated to 220 °C (c) compound [V]<sub>3</sub> on cooling at 180 degrees (d) compound [V]<sub>4</sub>'s phase 4 was achieved after heating to 190 °C (at 200 x magnification).



**Figure 3:** A graph of the alkoxy chain of  $[V]_n$  series of transition temperature against carbon atom count (n)

#### 4. Conclusions

Thiazolidine-2,4-dione with a core of 1,3-phenylene was used to create new symmetrical compounds. Molecular geometry and the length of flexible alkoxy units played the key roles in regulating the liquid crystal compound phase-transition properties.

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