Synthesis and structural determination of thermochromic compound

To Phuong Linh[1], Nguyen Minh Tri[1], Le Ngoc Hoan[1], Pham Van Nam[2], Vu Ngoc Toan[1*]

[1]Institute of New Technology/Academy of Military Science and Technology, 17 Hoang Sam, Cau Giay, Hanoi, Vietnam;
[2]Military Technical Academy, 236 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam.
[*]Corresponding author: vntoanchem@gmail.com
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ABSTRACT

Thermochromic materials are extensively utilized in various fields, such as healthcare, textiles, and military applications. The exceptional thermal properties of these materials are attributed to the thermochromic substances they contain. Lactone-based thermochromic compounds, known for their high sensitivity, broad color change range, and durability, have been extensively researched and developed. In this article, a thermochromic compound, crystal violet lactone (CVL), chemically identified as 3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide, was prepared through two steps by the reaction of N,N-dimethylaniline, m-dimethylaminobenzoic acid, and p-dimethylamino-benzaldehyde in acid condition. CVL exists in white powder, melting point 180 - 183 °C, yield 61.6%. The product structure was determined by modern physical methods such as IR, 1D NMR, 2D NMR, and MS spectra.

Keywords: CVL; Crystal violet lactone; Thermochromic compound; Thermochromic materials.

1. INTRODUCTION

Thermochromic materials have been researched, developed, and applied in many fields since the 1960s [1]. The color change mechanism is due to a change in structure or crystal phase when the temperature is low or high. Thermochromic compounds are classified into many groups, lactone thermochromic, such as CVL is widely used in industry, medical treatment, and other fields due to their unique properties. These compounds have rapid discoloration at low temperatures and good color recovery [2]. Many new materials can be created by using fibers, capsules, CVL, and pigments that react to heat stimulation in different materials. These materials have different characteristics and functions and are widely used in many applications, such as monitoring body temperature-changing for the medical industry or military camouflage [3].

CVL was first synthesized in 1978 by Maulding D. R. et al. [4]. The method included the condensation of Michler's hydrol to form Leuco crystal violet lactone (LCVL), chemically identified as 2-[4,4'-bis(dimethylamino)benzyhydryl]-5-dimethylaminobenzoic acid, and oxidation of LCVL to CVL. Yang N.F. et al. proposed the synthesis of CVL by using *N*,*N*-dimethylaniline, *m*-dimethylaminobenzoic acid, *p*-dimethylaminobenzaldehyde with acid catalysis (HCl) under the protection of nitrogen [5]. Myeong Jin et al. synthesized CVL from phthalic anhydride and 4-phenylmorpholine, catalyzed by anhydrous $AlCl_3$ [6]. However, the above methods have low yields and complicated processes, making it difficult to scale up production. In this article, we successfully synthesized CVL using a new and simple method with a relatively high yield. The product's structure was evaluated as a basis for its application on fabric surfaces in military camouflage.

2. EXPERIMENT

2.1. Materials and equipment

Materials: *N,N*-dimethylaniline (99%, was provided by Xilong Scientific, China); *m*-dimethylamino benzoic acid (99%, was provided by Macklin, China); *p*-dimethylamino benzaldehyde (99%, was provided by Xilong Scientific, China); sodium hydroxide (99%, was provided by Xilong Scientific, China); Hydrochloric acid (37%, was provided by Duc Giang Co., Vietnam); Toluene (was supplied by Fisher); sulfuric acid (98%, was supplied by Fisher); potassium persulfate (99%, was provided by Xilong Scientific, China).

Equipment: Melting point (uncorrected) is measured on STUART SMP3 (BIBBY STERILIN-UK). The FTIR-spectra was recorded on Tensor II Bruker (Germany) in the form of KBr. The 1D and 2D NMR spectra were recorded on an Advance NEO (Bruker, Germany). Analytical balance 300 g, error ± 0.001 g (Labex, China); magnetic stirrer with heating, maximum stirring speed 1500 rpm, heating up to 370 ^{o}C (Velp ARE, Italy); filter paper Ø 18 cm (NewStar, China).

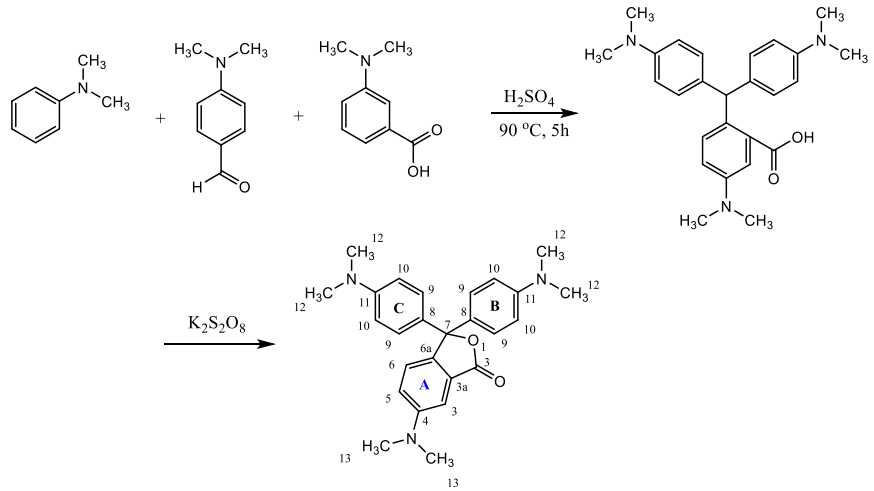
2.2. Process for the preparation of Crystal violet lactone (CVL)

- Step 1: Preparation of leuco crystal violet lactone (LCVL): 3-(dimethylamino)benzoic acid (1.5 g), 4-(dimethylamino)benzaldehyde (1.8 g), and urea (0.6 g) are dissolved in *N,N*-dimethylaniline (2 mL). This mixture is refluxed for 12 hours, then cooled and extracted with 20 mL of toluene (×3). The aqueous layer was acidified with hydrochloric acid to precipitate the product. Then, 2.5 g of leuco crystal violet lactone (LCVL) was obtained (78.2% yield).

- Step 2: Oxidation LCVL to CVL: A solution of 2.5 g LCVL in sodium hydroxide (1.5 g of 50% NaOH in 30 mL water) is extracted twice with 15 mL of toluene at (60 - 70) ^{o}C. The extracted aqueous solution is heated to 60 ^{o}C, and an aqueous solution of 1.9 g of potassium persulfate in 20 mL of water is slowly added to that over 60 minutes. The resulting white solid are filtered by Buchner funnel, washed with 50 mL of hot (60 - 70 °C) water, and dried. 1.53 g of crystal violet lactone was obtained (61.6% yield). The product was purified by column chromatography with a solvent system of petroleum ether: ethyl acetate = 17:3, melting point 180 - 183 ^{o}C.

3. RESULTS AND DISCUSSION

The reactions in the synthesis of CVL are presented in scheme 1.



Scheme 1. *Synthesis path for CVL.*

The structure of the product was confirmed by using the IR spectroscopic method. The IR spectrum of the product appears as the absorption band of the functional groups present in the molecule. The characteristic IR spectra regions are 2900-2800 cm^{-1} (ν_{CH}), and the strong absorption band at 1742 cm^{-1} is characterized by the group C=O of a 5-membered lactone ring linked to an aromatic double ring. The absorption bands at 1192 cm^{-1} and 1075 cm^{-1} are characterized by the asymmetric and symmetric valence vibrations of the C-O (ether) bond. The absorption bands at 1608, 1518, and 1485 cm^{-1} are characterized by the C=C bond vibrational value in the aromatic ring. In addition, the appearance of a strong absorption band at 809 cm^{-1} is characterized by the 1,4-substitution of the two aromatic rings B and C.

The assignment of protons and carbons in the molecule of product is based on the following spectral data:

- The weakest resonance signal appears at δ = 170.0 ppm and is assigned to carbon in the C=O group (lactone).

- ^{1}H NMR spectrum: The resonance signal appears at δ = 7.13 ppm with dd multiplicity, spin-spin interaction constants J_1 = 9.0 Hz and J_2 = 2.4 Hz indicate that they interact with protons at positions other than *ortho* and *meta*. Therefore, this proton can be assigned to H-5. This is the key signal to finding the other protons and carbons in the molecule. Resulted COSY spectrum of CVL shows the resonance signal at δ = 7.13 ppm interacts with 2 signals at δ = 7.41 ppm and δ = 6.97 ppm. As a result, it can be attributed to these 2 signals of H-6 (J_{ortho} = 9.0 Hz) and H-3 (J_{meta} = 2.4 Hz), respectively. Observing the HSQC interaction spectrum, it can be indicated that the signals at δ = 7.41 ppm (H-6), δ = 7.13 ppm (H-5) and δ = 6.97 ppm (H-3) have close interactions with carbon at δ = 124.4 ppm, δ = 119.1 ppm and δ = 105.5 ppm respectively which can be assigned to the carbon atoms at C-6, C-5 and C-3 respectively.

- HMBC spectrum: The resonance signal of proton H-6 at δ = 7.41 ppm has a long-range interaction with the two carbon signals at δ = 150.9 ppm and δ = 125.7 ppm. On the other hand, the signal at δ = 150.9 ppm has a long-range interaction with the proton at δ = 2.97 ppm. Therefore, the signal at δ = 150.9 ppm can be determined to be that of the C-4 carbon, and the signal at δ = 2.97 ppm to be that of the H-13 proton. From the HSQC spectrum, C-13 is determined similarly in the signal at δ = 40.1 ppm. Also, in the HMBC spectrum, the H-5 proton signal has a long-range interaction with the two resonance signals of carbon at δ = 140.4 ppm and δ = 105.5 ppm (C-3). Thus, the signal at δ = 140.4 ppm is from carbon C-6a. The remaining signal in aromatic ring A at δ = 125.7 ppm is attributed to carbon H-3a.

- COSY spectrum: A pair of near H-H interactions of the two signals appear at δ = 7.04 ppm and δ = 6.66 ppm. The resonance signal at δ = 6.66 ppm is affected by the effect of electron expulsion into the ring from the N-$(CH_3)_2$, shifting towards the stronger field compared to the signal at δ = 7.04 ppm. As a result, the signals at δ = 7.04 ppm and δ = 6.66 ppm are assigned to H-9 and H-10, respectively. From these two proton signals, combined with the HSQC spectrum, we found 2 corresponding carbon signals of C-9 and C-10 at δ = 127.5 ppm and δ = 111.7 ppm. Observation of the HMBC spectrum shows that the signal of H-9 has a long-range interaction with the carbon signal at δ = 149.9 ppm. It can be assigned to carbon C-11, which has a long-range interaction with the proton at δ =

2.86 ppm, so this is the H-12 proton. Carbon C-12 at δ = 39.9 ppm was also determined by the resulting COSY spectrum of CVL.

- Observing the HMBC spectrum of the product, the resonance signal of proton H-9 at δ = 7.04 ppm has a long-range interaction with the signal at δ = 91.4 ppm. Therefore, this is carbon C-7. The last carbon signal in the molecule at δ = 128.9 ppm is C-8.

The HSQC and HMBC spectra of the product are presented in the table below.

Table 1. *Resulted in HSQC and HMBC spectra of product.*

2D NMR ^{1}H-^{13}C HSQC of product		**2D NMR ^{1}H-^{13}C HMBC of product**	
Carbon-13 (δ, ppm)	**Proton (δ, ppm)**	**Carbon-13 (δ, ppm)**	**Proton (δ, ppm)**
127.5 (C-9)	7.04 (H-9)	150.9 (C-4)	7.41 (H-6), 40.1 (C-13)
124.4 (C-6)	7.41 (H-6)	149.9 (C-11)	7.04 (H-9), 2.86 (H-12)
119.1 (C-5)	7.13 (H-5)	140.4 (C-6a)	7.13 (H-5), 6.97 (H-3)
119.1 (C-10)	6.66 (H-10)	128.9 (C-8)	6.66 (H-10)
105.5 (C-3)	6.97 (H-3)	127.5 (C-9)	7.04 (H-9)
40.1 (C-13)	2.97 (H-13)	125.7 (C-3a)	7.41 (H-6)
39.9 (C-12)	2.86 (H-12)	119.1 (C-5)	6.97 (H-3)
-	-	119.1 (C-10)	6.66 (H-10)
-	-	105.5 (C-3)	7.13 (H-5)
-	-	91.4 (C-7)	7.04 (H-9)

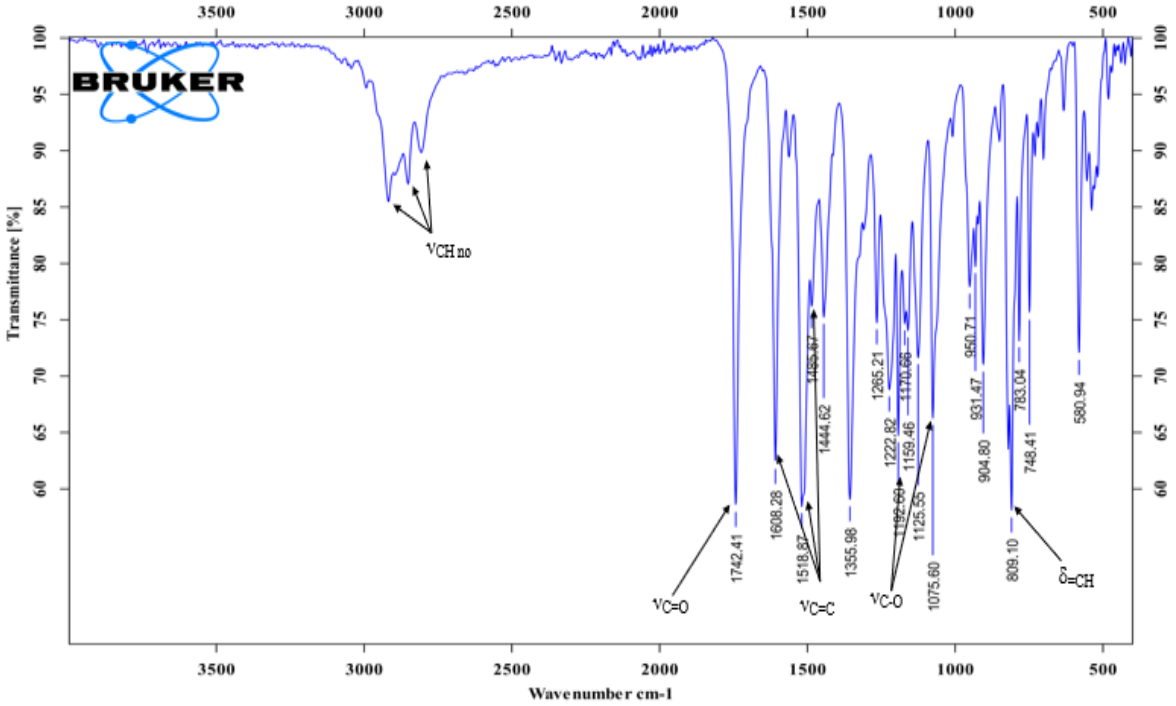


Figure 2. *IR spectrum of product.*

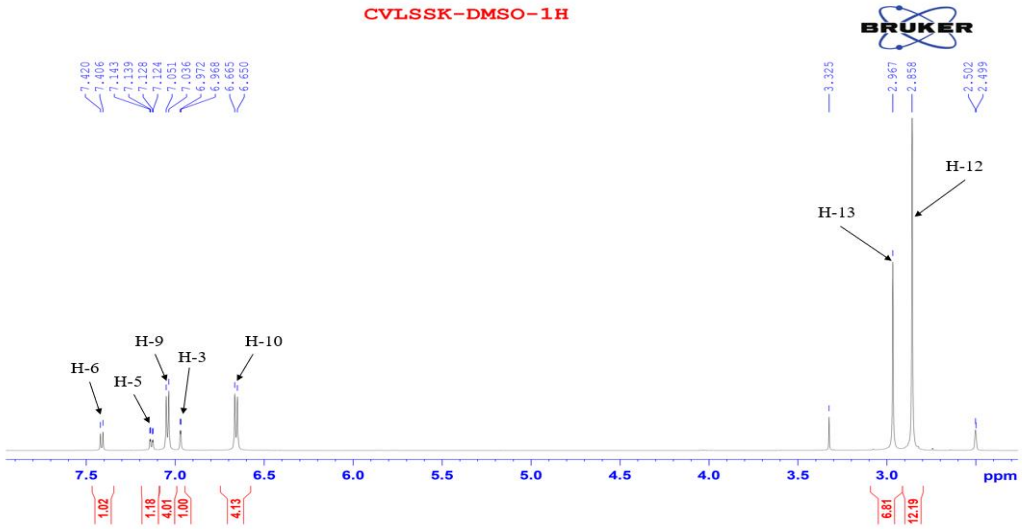


Figure 3. *^{1}H NMR spectrum of product.*

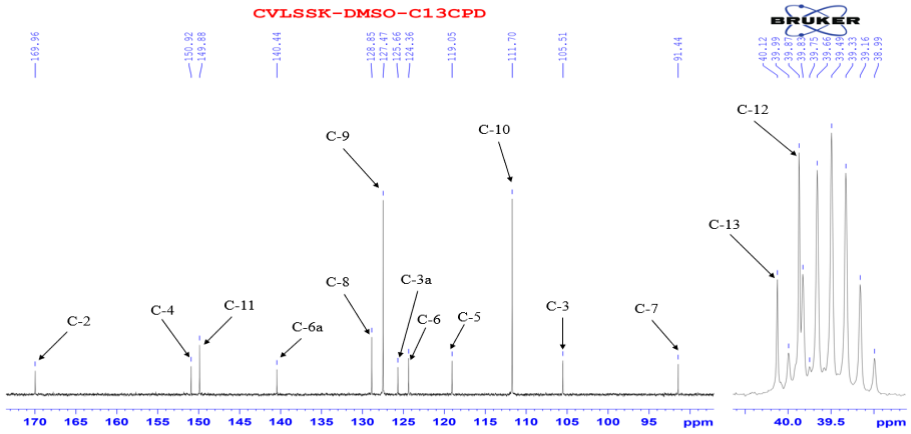


Figure 4. *^{13}C NMR spectrum of product.*

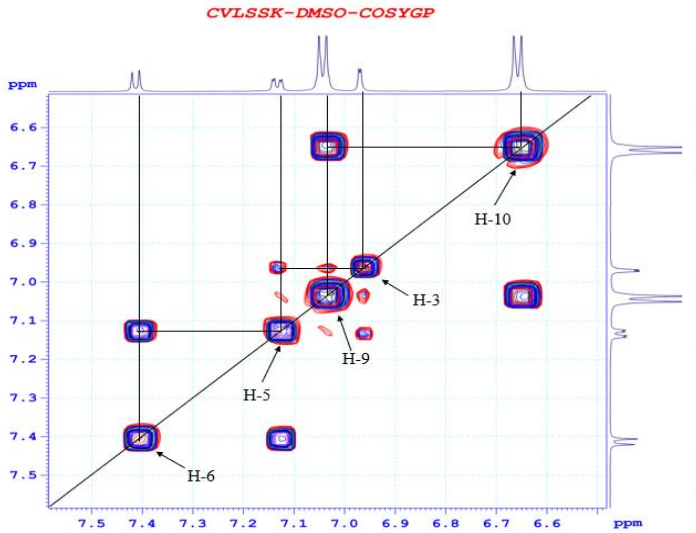


Figure 5. *COSY spectrum of product.*

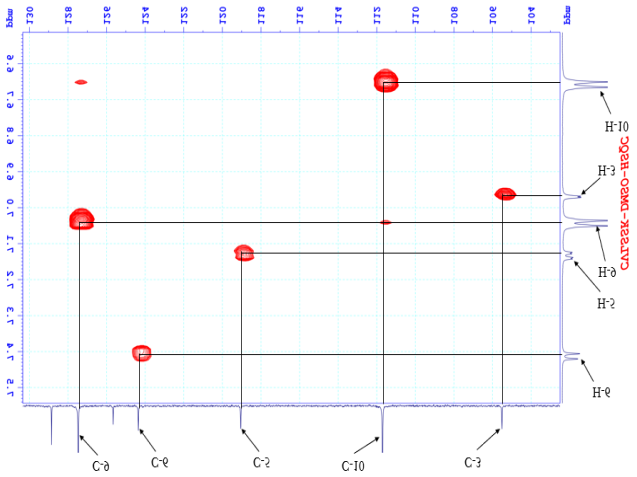


Figure 6. *HSQC spectrum of product.*

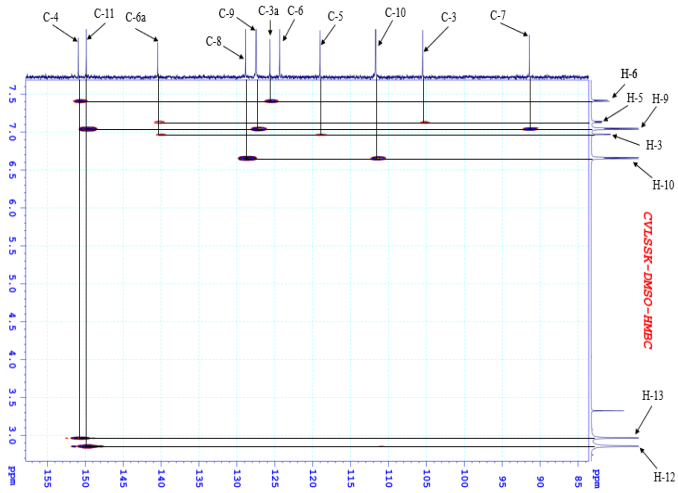


Figure 7. *HMBC spectrum of product.*

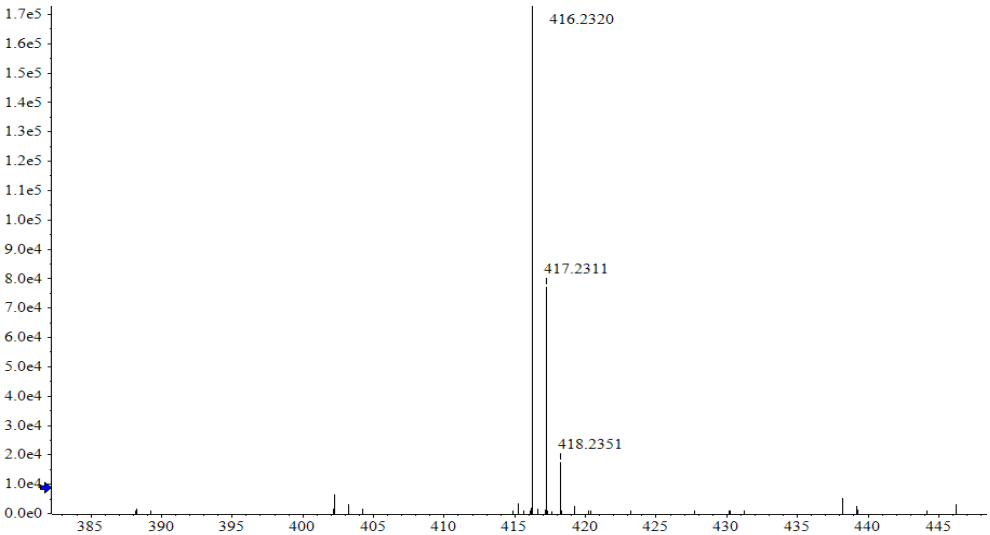


Figure 8. *MS spectrum of product.*

MS spectrum of product was measured by ESI method. On the ESI-MS spectrum, the molecular ion peak appears with a mass number consistent with the calculated molecular weight of the compound. In the spectrum, the molecular ion peak [M^+] appears at mass number m/z = 416.232 in accordance with the calculated value of molecular weight, M=416.233 Da, for the corresponding molecular formula $C_{26}H_{29}N_3O_2$ with M (calculated)=416.233 Da. In addition, the spectrum also shows some pseudo-molecular ion peaks $[M+H]^+$ and $[M+2H]^+$ with m/z = 417.2311 and 418.2351, respectively.

The results of the melting point, IR spectrum, ^{1}H NMR, ^{13}C NMR, COSY, HSQC, HMBC, and MS spectra of product show that we successfully synthesized CVL and accurately determined the structure of this product.

4. CONCLUSIONS

The thermochromic compound CVL was synthesized by a simple two-step reaction. The structure of the product was determined by modern spectroscopic methods. The results showed that the obtained product had a molecular structure consistent with the expected structural formula.

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TÓM TẮT

Tổng hợp và xác định cấu trúc chất nhiệt sắc

Vật liệu nhiệt sắc được sử dụng phổ biến trong các lĩnh vực: y tế, dệt may và quân sự. Các tính chất nhiệt độc đáo của vật liệu này do thành phần chất nhiệt sắc của vật liệu đem lại. Các chất nhiệt sắc họ lactone được sử dụng phổ biến vì có khoảng nhiệt độ thay đổi màu rộng, độ nhạy và độ bền cao. Trong nghiên cứu này, một loại chất nhiệt sắc họ lacton là crystal violet lactone (CVL) được tổng hợp bằng phản ứng giữa các thành phần N,N-dimethylaniline, m-dimethylaminobenzoic acid và p-dimethylamino-benzaldehyde trong môi trường acid qua hai giai đoạn. Sản phẩm thu được ở dạng rắn, màu trắng, nhiệt độ nóng chảy 180 - 183 ^oC với hiệu suất đạt 61,6%. Cấu trúc của sản phẩm sau tổng hợp được xác định bằng các phương pháp vật lí hiện đại như IR, 1D NMR, 2D NMR và MS.

Từ khóa: CVL; Crystal violet lactone; Chất nhiệt sắc; Vật liệu nhiệt sắc.