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Synthesis of Benzimidazole Sweat Fingerprint Fluorescent Developer and Fluorescent Effect

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In this paper, benzimidazole fluorescent compounds (compound 1 and compound 2) containing hydroxymethyl and carboxyl substituents were synthesized by replacing salicylaldehyde and substituted ortho-phenylenediamine.By measuring the spectral properties of these fluorescent compounds, the influence of different substituents on the fluorescence properties of these fluorescent compounds was investigated and the fluorescence effect of these fluorescent compounds as a fluorescent latent agent for sweat fingerprinting was also investigated.The obtained hydroxymethyl and carboxyl substituted benzimidazole sweat latent fingerprints have good adsorption performance, remarkable fluorescence effect and strong stability, therefore, they can be widely used.This research also expands the research and application range of benzimidazole derivatives and it has very important research value in the field of criminal detection technology.

1. Introduction

Fingerprint refers to the pattern that human left with fingers on the surface of the object. In forensic science, many technologies have so far been developed for latent perspiration fingerprints (Sheng et al., 2011), which comprise only two types on account of its morphology. The one is to detect sweat latent fingerprint on a porous surface such as papers based on ninhydrin and 1,8-diaza-9-fluorenone (DFO). The second type is just the other way around, i.e. to get it on the non-porous surfaces such as glass and plastic based on cyanoacrylate smoke. As applied widespread at crime scenes, both require cumbersome pretreatment such as luminescent dye spray and vacuum metal deposition to recur the latent fingerprints high visibly (Xu, et al., 2012). For this reason, some simpler, more convenient and more reliable fingerprint detection technologies are in dire need (Kwak et al., 2009). It is found that various fluorescent developers can be used as the most ideal method to dispose latent perspiration fingerprints (Li et al., 2013.). Fluorescent developer for fingerprint color development is a non-destructive technology that not only requires minimal sample preparation, but also reduces the propability of fingerprint contamination, thus increasing the efficiency of sample analysis.

Fluorescence detection as a common used method features easy sampling, less samples, easy to operate and so on. Samples can be tested and analyzed based on many data about excitation spectrum, emission spectrum, fluorescence quantum yield, fluorescence lifetime and displacement (Tang et al., 2013). Benzimidazoles compound is an important class of fluorescent molecular material, due to its special structure and good reactivity, it can emit characteristic fluorescence spectra with large displacement and high fluorescence quantum yield. Beyond that, it is due to easy formation of a complex. when it reacts with transition metal ions that its fluorescence properties change, which thus leads to a continuity recognition (Liu et al., 2011). Therefore, benzimidazole compounds are widely used in the field of fluorescence detection.

1.1 Synthesis Mechanism of Benzimidazole compounds

In 1997, Porai-Koshits and colleagues proposed a reaction mechanism for the formation of benzimidazole compound from the ring-closure of organic acids and o-phenylenediamine, namely the reaction mechanism the the Michael addition synthesizes benzimidazolyl-carboxylic acids, as shown in Fig. 1;

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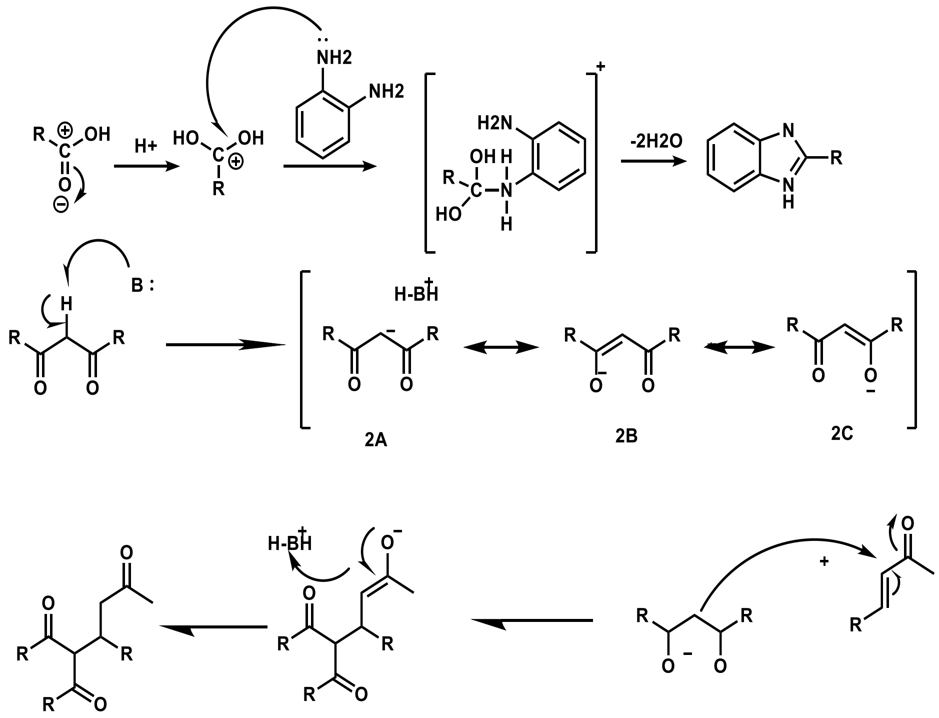

Figure 1: Reaction mechanism of benzimidazoles

1.2 Mechanism of fluorescence generation

Electrons exist in ground state and in excited state, in general, those in former state are more stable than those in the latter. Fluorescence refers to the optical energy unleashed by molecule or atom in an excited state during its return to the ground state (Shen et al., 2010). Electron in the molecules moves constantly in a different state that corresponds to various energy states, that is, energy levels. Those electrons disperse in different energy levels. In the absence of external energy absorption, the electron stays at the lowest level, that is, the ground state most stably. In some cases, for example, when a molecule is heated or exposed to illumination, the electron in the ground state absorbs energy and steps from the ground state to the other high energy levels, i.e. the electron transition process just as everyone knows. At this time, the electron falls in an excited state, and looks very unstable. It easily unleashes the energy to return to the ground state. When the electron in the excited state jump to the ground state again, the energy it has absorbed when being excited will be released in the forms of heat and light. When electrons unleash energy in the form of thermodynamics, it is called non-radiative transitions. When electrons release energy in the form of illumination, this process is called a radiative jump. When this is the case, it will emit light, this process is called emission. Electrons in the excited state are generally singlet more unstably and with short half-life period. The electrons release energy by way of radiation when they return from the singlet excited state to the ground state, they emit light within extremely short time, called a fluorescence (Zhuang, 2013).

In order to fill up the gap of the above detection technologies for latent perspiration fingerprints and in allusion to the good fluorescence properties of benzimidazole compounds, this paper proposes the synthesis of a series of benzimidazole fluorescence compounds containing hydroxymethyl and carboxyl substituent groups with substituted salicylaldehyde and o-phenylenediamine as raw materials (Kim et al., 2013). By measuring the spectral properties of these fluorescent compounds in ethyl alcohol, this study focuses on what is the impact of the different substituents on luminescent property of these fluorescent compounds, and what is the fluorescence effect of them when being applied as fluorescent developer for latent perspiration fingerprints.

2. Experiments

2.1 Test equipment and reagents

Test equipment and reagents required for synthesizing these benzimidazole fluorescent developer are listed in Table 1.

Table 1: test equipment and reagents required

Test equipments		The main test reagents	
Equipments	Manufacturer	Reagents	Manufacturer
Magnetic heating stirrer	Shenzhen Sha Kok Kok Guohua Instrument Factory	Salicylaldehyde	Shanghai Reagent Co., Ltd.
Circulating water pump	Shanghai Ya Rong Biochemical Instrument Factory	1,4-dioxane	Shanghai Reagent Co., Ltd.
Rotary evaporator	Shanghai Ya Rong Biochemical Instrument Factory	Concentrated hydrochloric acid	Shanghai Reagent Co., Ltd.
Vacuum oven	Tianjin Sanshui Scientific Instrument Factory	Glacial acetic acid	Shanghai Reagent Co., Ltd.
Electronic balance	Shanghai Jingke balance factory	acetone	Shanghai Reagent Co., Ltd.
UV absorption spectrometer	Hitachi Co.,Ltd.	N,N-dimethylformamide	Shanghai Reagent Co., Ltd.
Fluorescence spectrophotometer	Hitachi Co.,Ltd.	Formaldehyde solution	Shanghai Reagent Co., Ltd.
Nuclear magnetic resonance	Bruker DRX-400Hz	hydrogen peroxide	Shanghai Reagent Co., Ltd.

2.2 Synthesis of benzimidazole fluorescent developer

0.125 mol salicylaldehyde and 0.075 mol paraformaldehyde are added to 100 ml concentrated hydrochloric acid, seal up and let them react at room temperature. After 48 hours, a large amount of white solids generates. Remove the solvent with vacuum filtration and wash the resultant solids immediately with an appropriate amount of ethyl acetate for three times, then discard the aqueous layer and dry the ethyl acetate layer over anhydrous magnesium sulfate. Remove desiccant by filtration in vacuo, and clear up solvent by reduced pressure distillation, and then the rest is recrystallized into white needle-like crystal using a mixed solvent of petroleum ether and ethyl acetate (1: 1). Mix such crystal (0.02 mol) with 20 m L absolute ethanol, stir the mixture for 4 h at room temperature, and add 20 m L methylene chloride and 0.02 mol o-phenylenediamine, heat them up to run reflux reaction for 3 h. After the reaction is ended, the reaction solution as cooled is poured into 400 ml ice water, allow it to stand and then filter it in vacuum. the last solid is recrystallized in absolute ethanol into a solid powder which is so called the target benzimidazole fluorescent developer (Jayabharath, et al., 2013; Tae, et al., 2007). Repeat the above compound 1 procedure for Compounds 2. The specific synthsis pathway is shown in Fig. 2 and 3.

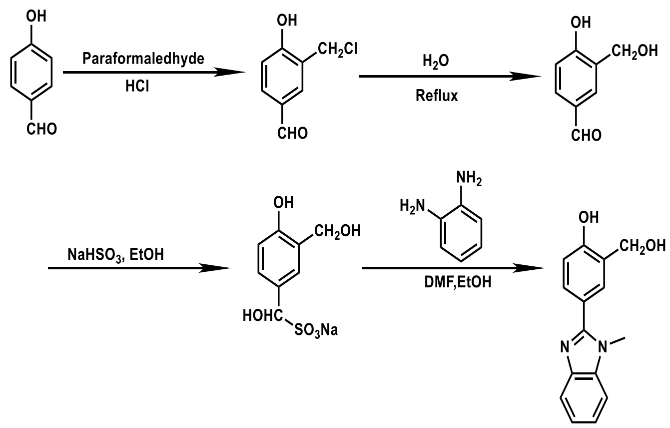

Figure 2: Synthesis of hydroxymethyl-substituted benzimidazoles (Compound 1)

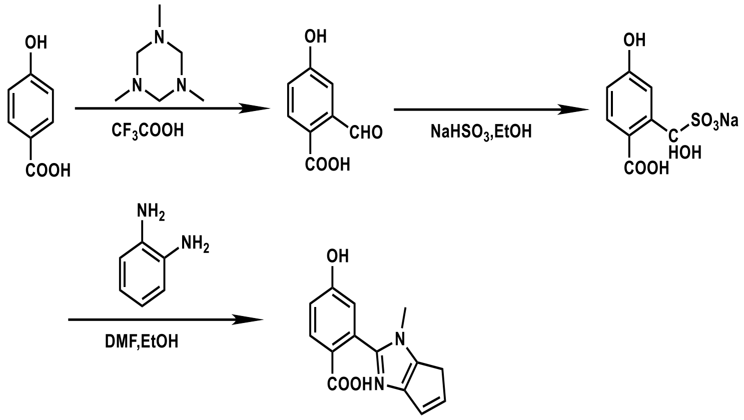

Figure 3: Synthesis of carboxy-substituted benzimidazoles (Compound 2)

2.3 Analysis on elements, infrared spectroscopy and nuclear magnetic resonance of benzimidazole fluorescent developer

2.3.1 Elements

The elements of synthesized benzimidazole fluorescent developer are analyzed with experimental and theoretical values in Table 2.

Table 2: Elemental analysis data of benzimidazole-type fluorescent imaging agent

Compound 1			Compound 1		
Element	Theoretical calculation /%	Measured value /%	Element	Theoretical calculation /%	Measured value /%
C	64.21	64.19	C	55.92	55.94
H	11.97	11.96	H	21.64	21.61
N	9.42	9.45	N	8.89	8.91

2.3.2 Infrared spectroscopy

The infrared spectroscopy of synthesized benzimidazole fluorescent developer is analyzed with main characteristic peaks obtained as shown in Table 3.

Table 3: IR spectra of Compound 1 and Compound 2 Characteristic absorption frequency

Compound	Characteristic absorption peak					
1	vC-H (Ph)	N C=N (Imid)	vC-N(Ph)	vC-O-C(PhOSO3)	vC-H(p-Ph)	vC-H(o-Ph)
	3065.29	1459.09	1372.08	1104．34 879.38	883.32 891.04	742.02 776.75
2	vC-H (PhOH)	vC=N (Imid)	vC-H(p-Ph)	vC-H(o-Ph)	vC-N(Ph)	vC-C(CHO)
	3309.67	1476.87	865.97	773.75	1302.86	3183.74

2.3.3 Nuclear magnetic resonance

The nuclear magnetic resonance of synthesized benzimidazole fluorescent developer is analyzed with 1H NMR spectrum as shown in Fig. 3.

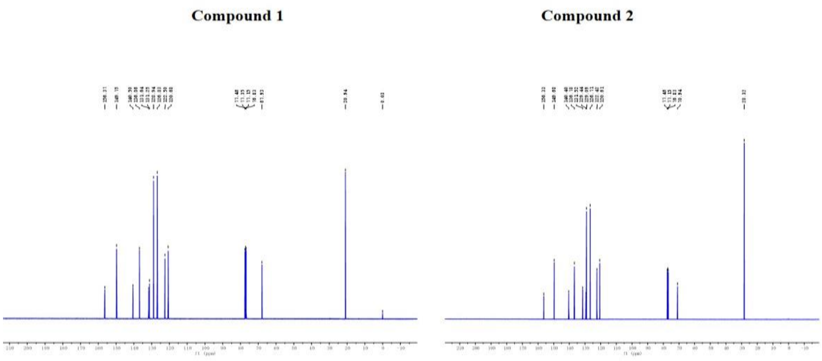

Figure 4: 1H NMR spectrum of Compound 1 and Compound 2

It can be seen from Fig. 4 that the types of hydrogen in compound 1 and compound 2 are consistent with the theoretical value.

3. Fluorescence Study of Sweat latent fingerprints fluorescent agent with the structure of Benzimidazole

The newly synthesized benzimidazole fluorescent developer is used to recur the fingerprints so that the following phenomena can be revealed. ①The new benzimidazole fluorescent developer sharpens the fingerprints and the detail features. ②The novel benzimidazole fluorescent developer evenly adheres to the sweat latent fingerprints presented on the objects, which makes the fingerprint streakline smooth and coherent. ③Novel benzimidazole fluorescence developer can be used as a the excitation light source for the ordinary shortwave ultraviolet light and multi-band light source, while it is cheap, not required to heat it up, compared to other fingerprint fluorescent developers, it is more simple and easy to operate. ④New benzimidazole fluorescent developer can reveal fingerprints on the permeability and impermeability substrates, so widely applied. ⑤In relation to the conventional sweat latent fingerprint developer DFO (Fig. 5c), the new benzimidazole sweat latent fluorescent developer has been proven to be better on the latent sweat fingerprints due to many features such as clearness, and prominent details (Fig. 5a and 5b), smooth and coherent streaklines. This fluorescent developer can be used as the excitation light source for the ordinary shortwave UV lamp and multi-band light source, and available at a low price. It does not requires to heat the fingerprint up, simplicity and easy to operate, hence is widely applied in the world.

Figure 5: The fingerprints of novel benzimidazole sweat latent compound 1(a), compound 2 (b) and DFO (c)

4. Conclusion

In this dissertation, substituted benzalimidazole compounds containing hydroxymethyl and carboxyl substituents were synthesized by replacing salicylaldehyde and substituted ortho-phenylenediamine.By measuring the spectral properties of these fluorescent compounds, the influence of different substituents on the fluorescence properties of these fluorescent compounds was investigated and the fluorescence effect of these fluorescent compounds as a fluorescent latent agent for sweat fingerprinting was also investigated.The obtained hydroxymethyl and carboxyl substituted benzimidazoles sweat latent fingerprints have good adsorption properties and can show good fluorescence in the range of 350-700 nm and still have good fluorescence in the tracking months effect; At the same time, the reaction starting materials of the benzimidazole fluorescent agent which synthesizes the hydroxymethyl and carboxyl substituents are easy to obtain, the cost is low, the reaction steps are relatively simple, the reaction conditions are relatively mild, and the yield of the whole reaction is also high , The resulting product fluorescence significant effect, strong stability, therefore, can be widely used. Meanwhile, this research also expands the research and use range of benzimidazole derivatives and has very important research value in the field of criminal detection technology. The benzimidazole sweat latent fluorescent agent containing hydroxymethyl and carboxyl substituent and its application performance deserve further study.

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