Synthesis and Characterization of 1,4-Dibromo-5H-benzo[a]phenothiazin-5-one and 8,13-Dibromo-7H-naphtho[2,3-a]phenothiazin-7-one for Use as Novel Fingermark Visualisation Reagents

[1]Kıymet Berkil Akar*, [2]Oğuzhan Bebek and [2]Barış Eran
[1]*Department of Chemistry, Faculty of Science and Letters, Tokat Gaziosmanpaşa University, Tokat, TR-60250, Türkiye.*
[2]*Department of Bioengineering, Faculty of Engineering and Architecture, Tokat Gaziosmanpaşa University, Tokat, TR-60150, Türkiye.*
kiymet.berkilakar@gop.edu.tr*

(Received on 2nd February 2023, accepted in revised form 13th September 2023)

Summary: In the presented study, novel compounds bearing the benzo[a]phenothiazine or naphtho[a]phenothiazin skeletons were developed for the first time as fingermark detecting reagents on paper surfaces which were then investigated in detail. First, two phenothiazine derivatives, 1,4-dibromo-5H-benzo[a]phenothiazin-5-one and 8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one were synthesized and characterized by spectroscopic methods. The phenothiazines were tested as potential reagents for latent fingermarks on copier paper and were then compared with 1,8-diazofluoren-9-one (DFO). Both compounds reacted with latent fingermarks on the paper to yield photoluminescent prints with high contrast and quality and were slightly inferior to DFO. In addition, the results also revealed that they could also develop fingermarks aged up to three-months.

Keywords: Latent fingermark, Phenothiazine, Synthesis, DFO, Copier paper, Amino acid

Introduction

Fingermarks are one of the most valuable physical evidences commonly used for personal identification in forensic investigations [1-3]. Most fingermarks collected during forensic investigations are latent fingermarks consisting predominantly of natural skin secretions [4]. The composition of natural skin secretions is a mixture of numerous substances such as glycerides, fatty acids, amino acids, proteins, ions (Na^+, K^+ etc.) and trace metals (Cu, Zn etc.) [5, 6]. Detection of latent fingermarks is based on the reactions of fingermark reagents with certain substances such as amino acids and lipids in the fingermark secretions. Amino acid sensitive fingermark reagents such as ninhydrin, which can be used on porous surfaces, target stable components in the fingermark residue and therefore their effectiveness is less dependent on the age of the fingermark [7-9]. The exhibiting photoluminescence of the developed fingermarks is important in terms of increasing the detection sensitivity and contrast [7, 8], as well as allowing successful results with minimal fingermark secretion [10].

Fingermark reagents commonly used for porous surfaces in criminal laboratories are ninhydrin, DFO and 1,2-indandione [11]. Although ninhydrin creates very strong colour purple fingermarks in daylight, the developed fingermarks do not show luminescence, so additional processing is required. Unlike ninhydrin, these compounds are not suitable for use under daylight since fingermarks developed with DFO and 1,2-indandione are very pale pink traces to be seen under daylight although they form strong luminescent fingermarks [12].

Many studies have been carried out to develop new and effective fingermark reagents with superior properties to develop more fingermarks as evidence and improve their quality and quantity. Studies on producing new and effective fingermark reagents have mostly focused on the synthesis of ninhydrin derivatives [9, 13, 14]. In 2008, lawsone, a derivative of naphthoquinone, was first suggested as a fingermark reagent. Lawsone reacts with amino acids in skin secretions to form purple/brown fingermarks, which also exhibited photoluminescence [15]. Due to the good fluorescence properties of naphthoquinone derivatives, they have attracted considerable attention for use in the production of fluorescent chemosensors with high selectivity and sensitivity, as well as for use in the detection of latent fingermarks [16-19]. Recently, 1,4-anthraquinone derivatives have been investigated as alternative fingermark reagents. It was reported that the tested compounds were found to be inadequate as fingermark reagents [20]. More recently, 9,10-anthraquinones and 1,4-anthraquinones were investigated as potential fingermark reagents on paper surfaces. It has been reported that both 9,10-anthraquinones and 1,4-anthraquinones react with

*To whom all correspondence should be addressed.

amino acids to form faint yellow-orange fingermarks, which also exhibited photoluminescence. The results indicate that both 9,10-anthraquinones and 1,4-anthraquinones gave similar results to those of lawsone [10,21].

Phenothiazines are a class of active compounds containing electron-rich tricyclic nitrogen-sulphur heteroatoms (Figure 1) [22]. Many phenothiazine compounds show fluorescent properties [23]. In 1987, Fischer first studied phenothiazine as a fingermark reagent to developed latent fingermarks. In the proposed method, it has been reported that phenothiazine reacted with the oil material possible in the fingermark residue thus producing strong fluorescent fingermarks [24]. Plater and Harrison [25] reported that 3,7-dibromophenothiazin-5-ium (Figure 1) developed the latent fingermarks by forming pink or pale red product. They stated that the colour formed may be due to the formation of methylene blue analogue as a result of condensation of 3,7-dibromophenothiazine-5-ium with two equivalent amino acids [25]. Phenoxazines are also an important class of compounds that are structurally similar to phenothiazines. In the last thirty years, the use of Nile red (Figure 1), a derivative of phenoxazine, has been reported to detect lipid-rich latent fingermarks on wet porous surfaces and is effective in the development of fresh fingermarks [26-29].

The aim of the present study was to develop novel fingermark reagents for forensic investigations. Here we report the synthesis, characterization of two novel bromophenothiazine compounds and their performance as amino acid sensitive reagents. In addition, the performances of phenothiazines and DFO were comparatively examined. Finally, the performances of the phenothiazines in the development of aged fingermarks were also investigated.

Experimental

General

NMR spectra were recorded on a Bruker spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) and an Agilent spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C). High-resolution mass spectra were recorded on an Agilent 6210 spectrometer. The IR data were recorded on a Jasco FT/IR 430 instrument. HFE-7100^{TM} was purchased from 3M Novec (USA). All other chemicals have been purchased from Sigma Aldrich Company and used without any additional purification. Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh) column. TLC was performed on *DC-Alufolien* Keiselgel *60 F254* (Merck).

Chemistry

Synthesis of 1,4-dibromo-5H-benzo[a]phenothiazin-5-one (**3**)

K_2CO_3 (315 mg, 2.28 mmol) was added to a solution of 2-mercaptoaniline (104.6 mg, 0,836 mmol) in dichloromethane (25 mL) after which the mixture was stirred for 45 min at room temperature. At the end of this period, a solution of 2,5,8-tribromonaphthalene-1,4-dione (**1**) (0.3 g, 0.76 mmol) in dichloromethane (10 mL) was added dropwise to the mixture and stirring was continued at room temperature for additional 3 h. The resulting mixture was quenched with water (50 mL) and extracted with dichloromethane (3x50 mL). The combined organic layer was washed with water (100 mL) and dried over Na_2SO_4. The residue was crystallized from ethyl acetate/hexane (3 mL:1 mL) to give **3**.

1,4-dibromo-5H-benzo[a]phenothiazin-5-one (**3**)

Dark red needle crystals, yield 45% (142 mg), mp 199-201 °C; R_f= 0.51 (ethyl acetate-hexane 1:3); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J*= 6.6 Hz, 1H, ArH), 7.80 (d, *J*= 8.4 Hz, 1H, ArH), 7.72 (d, *J*= 8.4 Hz, 1H, ArH), 7.45-7.40 (m, 2H, ArH), 7.36 (d, *J*= 6.6 Hz, 1H, ArH), 6.72 (s, 1H, olefinic proton); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 177.3, 144.0, 139.2, 138.0, 137.5, 136.4, 134.2, 132.8, 132.5, 130.6, 127.8, 124.8, 122.7, 122.3, 120.9, 120.8; IR (ν_{max}, cm^{-1}) 3094, 3046, 2954, 2924, 2854, 1632, 1567, 1545, 1518, 1425, 1355, 1283, 1251, 1228, 1148, 1123, 1075, 950, 900, 851, 826, 763, 723, 646, 548, 503, 478, 431, 416; HPLC-TOF/MS m/z 419.9 $[M]^{+}$.

Synthesis of 8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**)

Triethylamine (TEA) (204 mg, 2.02 mmol) was added to a solution of 2-mercaptoaniline (93 mg, 0,741 mmol) in chloroform (15 mL) and the resulting mixture was stirred for 45 min at reflux temperature. At the end of this period, a solution of 2,9,10-tribromo-1,4-anthraquinone (**2**) (0.3 g, 0.67 mmol) in chloroform (10 mL) was added dropwise to the mixture and stirring was continued at reflux temperature for additional 6 h. The resulting mixture was quenched with water (50 mL) and extracted with chloroform (3x50 mL). The combined organic layer was washed with water (100 mL) and dried over Na_2SO_4. The residue was chromatographed on a short silica gel column using a mixture of ethyl acetate/hexane (1:9) as an eluent and crystallized from dichloromethane-hexane (3:1) to give **4**.

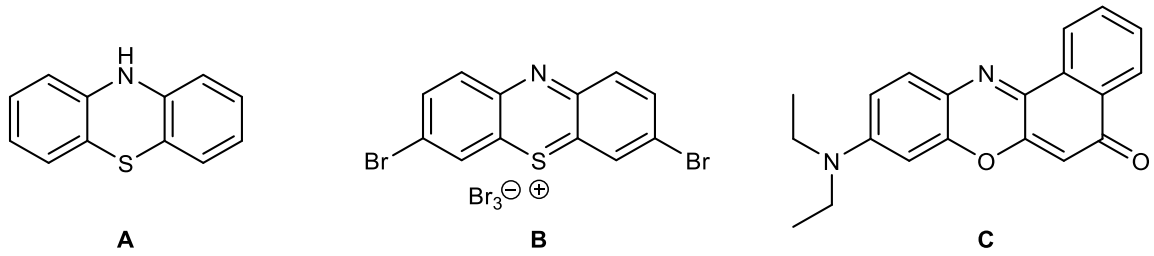

Fig. 1: Chemical structures of phenothiazine (**A**), 3,7-dibromophenothiazin-5-ium (**B**), and Nile red (**C**).

8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**)

Light orange needle crystals, yield 14% (44 mg), mp 230-232 °C, R_f= 0.54 (ethyl acetate-hexane 1:3); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.86-8.78 (m, 2H, ArH), 7.84-7.76 (m, 3H, ArH), 7.46-7.35 (m, 3H, ArH), 6.74 (s, 1H, olefinic proton); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 178.9, 146.8, 138.2, 137.9, 135.3, 134.9, 132.8, 131.6, 131.0, 130.9, 130.7, 130.6, 130.4, 130.3, 128.2, 125.6, 125.5, 125.0, 124.7, 122.6; IR (ν_{max}, cm^{-1}) 3049, 2947, 2923, 2855, 1620, 1562, 1543, 1469, 1444, 1372, 1321, 1306, 1244, 1166, 1150, 1118, 1040, 1027, 943, 879, 854, 840, 817, 785, 757, 741, 719, 695, 629, 556, 498, 473, 442, 420; HPLC-TOF/MS m/z 473.3$[M]^+$.

Preparation of Enhancing Solutions

The enhancing solutions were freshly prepared as indicated below:

DFO solution: DFO (0,25 g) was dissolved in methanol (40 mL), and acetic acid (20 mL) was added to this solution, stirring to produce a yellow solution. 940 mL of HFE7100 was added to this mixture and stirred [30].

Phenothiazine solutions:

- *1,4-dibromo-5H-benzo[a]phenothiazin-5-one (**3**) solution:* The *1,4-dibromo-5H-benzo[a]phenothiazin-5-one* (**3**) (30 mg) was dissolved in ethyl acetate (25 mL) and diluted with HFE-7100 solution (25 mL).
- *8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**) solution:* The 8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**) (25 mg) was dissolved in ethyl acetate (25 mL) and diluted with HFE-7100 solution (25 mL).

Sample Collection, Fingermark Development and Photography

Copier paper (80 g/m^2, Copier Bond) was used as the porous surface. Fingermarks were collected and aged for five different times periods (one-day, one-week, one-month, three-months, and six-months). 2 female and 6 males with ages ranging from 26-51 were selected as donors for the experiments. Fingermark tests were carried out with fingermarks from five different donors selected from among the donors for per experiment. Donors were requested to give fingermarks with their unwashed hands within at least half an hour in order to create natural fingermarks [31, 32]. Donors were asked to deposit a depletion series of 3 consecutive contacts with three fingers (index, middle and ring fingers) on copier paper with a contact time of 1 to 2 seconds and constant firm deposition pressure. Fingermarks were stored in a pp sheet protector before being treated. For comparison tests performed with different methods, fingermark series were cut in halves before dipping to the relevant solution.

The dipping method was used in the development of fingermarks. Each fingermark was dipped in enhancing solution in a glass tray for 10-15 s, then air-dried and heated in an oven (DFO: 100ºC for 20 min; phenothiazines: 170 ºC for 1h).

A negative control (copier paper without fingermark) and a positive control (copier paper on which an amino acid spot) treated with phenothiazines were included to validate the results. The positive controls were performed with an amino acid control system according to the literature method [21]. The amino acid solution (10 mL) was transferred to the copier paper, and the copier paper was allowed to air dry. All positive and negative control samples were dipped in phenothiazin solution in a glass tray for 10-15 s, left to air-dry and heated in an oven (170 ºC for 1 h).

The fingermarks and control samples were irradiated using the HandScope Xenon FLS 5000 forensic light source. Developed marks were photographed using a Nikon D3300 camera equipped

with a macro/close-up lens (Raynox MSN-202), and a red filter (Hoya R (25A)) under light at a wavelength of 440 nm. The wavelength of excitation has been decided by trying different wavelength values (365 to 615 nm) of the forensic light source.

Assessment of Developed Fingermarks

Centre for Applied Science & Technology (CAST) scale [33] was used to assess the relative performance of phenothiazines (**3** and **4**) and UC (University of Canberra) comparative scale [34] was used to assess the relative performance of two detection methods applied to split impressions.

Results and Discussion

Synthesis

Initially, 2,5,8-tribromonaphthalene-1,4-dione (**1**) and 2,9,10-tribromo-1,4-anthraquinone (**2**) were synthesized according to the literature method [35, 36]. We carried out substitution reactions of 2,5,8-tribromonaphthalene-1,4-dione (**1**) and 2,9,10-tribromo-1,4-anthraquinone (**2**) with 2-aminothiophenol in the presence of a base as shown in Figure 2. The target compounds, 1,4-dibromo-5H-benzo[a]phenothiazin-5-one (**3**) and 8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**), were synthesized with yields of 45% and 14%, respectively.

The yield is lower for 2,9,10-tribromo-1,4-anthraquinone (**2**). It can be stated that 2,9,10-tribromo-1,4-anthraquinone (**2**) is less reactive than 2,5,8-tribromonaphthalene-1,4-dione (**1**). Longer reaction time, higher temperature and strong base were required for this reaction. The reason is that the aromaticity of the aromatic part in the anthraquinone structure is less disturbed by the fused nonaromatic quinoid ring compared to naphthoquinone [37], and therefore it is a more stable compound.

The structures of the phenothiazines **3** and **4** were confirmed by ^{1}H-NMR, ^{13}C-NMR, IR, and HPLC-TOF/MS analysis. In the ^{1}H-NMR spectra of compounds **3** and **4** showed the presence of aromatic protons and an olefinic proton. The olefinic protons in the quinoid ring of **3** and **4** were observed as singlet at δ 6.72 and δ 6.74, respectively. The ^{13}C-NMR spectra of compounds **3** and **4** exhibited signals in the carbonyl, and aromatic regions. The carbonyl carbons of **3** and **4** were observed at δ 177.3, and δ 178.9, respectively.

Since the 2-aminothiophenol contained dual-nucleophilic centre (HS- and H_2N-), a cyclization product was formed instead of a substitution product. After the nucleophilic substitution reaction with the SH group, the other nucleophilic amine group attacks the carbonyl carbon resulting in intramolecular cyclization. Thus, 1,4-dibromo-5H-benzo[a]phenothiazin-5-one (**3**) and 8,13-dibromo-7H-naphtho[2,3-a]phenothiazin-7-one (**4**) were obtained as a result of nucleophilic substitution followed by an intramolecular cyclization as shown in Figure 3 below.

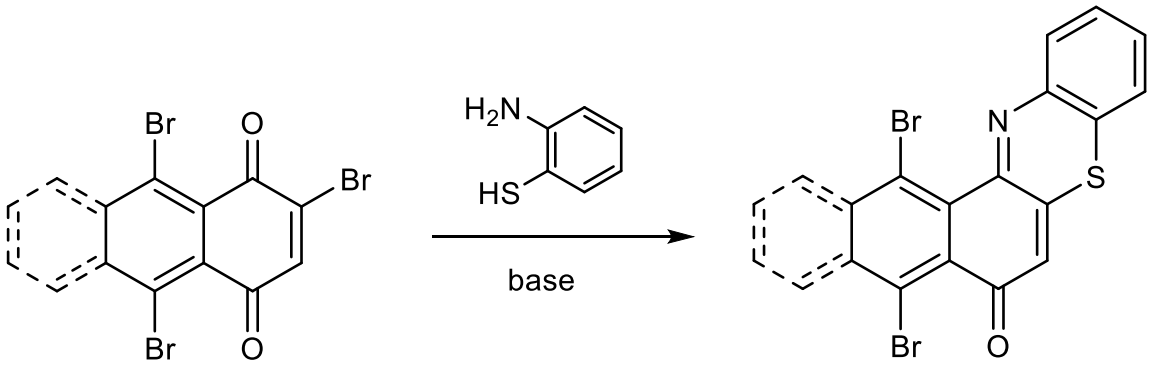

Fig. 2: Synthesis of phenothiazines **3** and **4**.

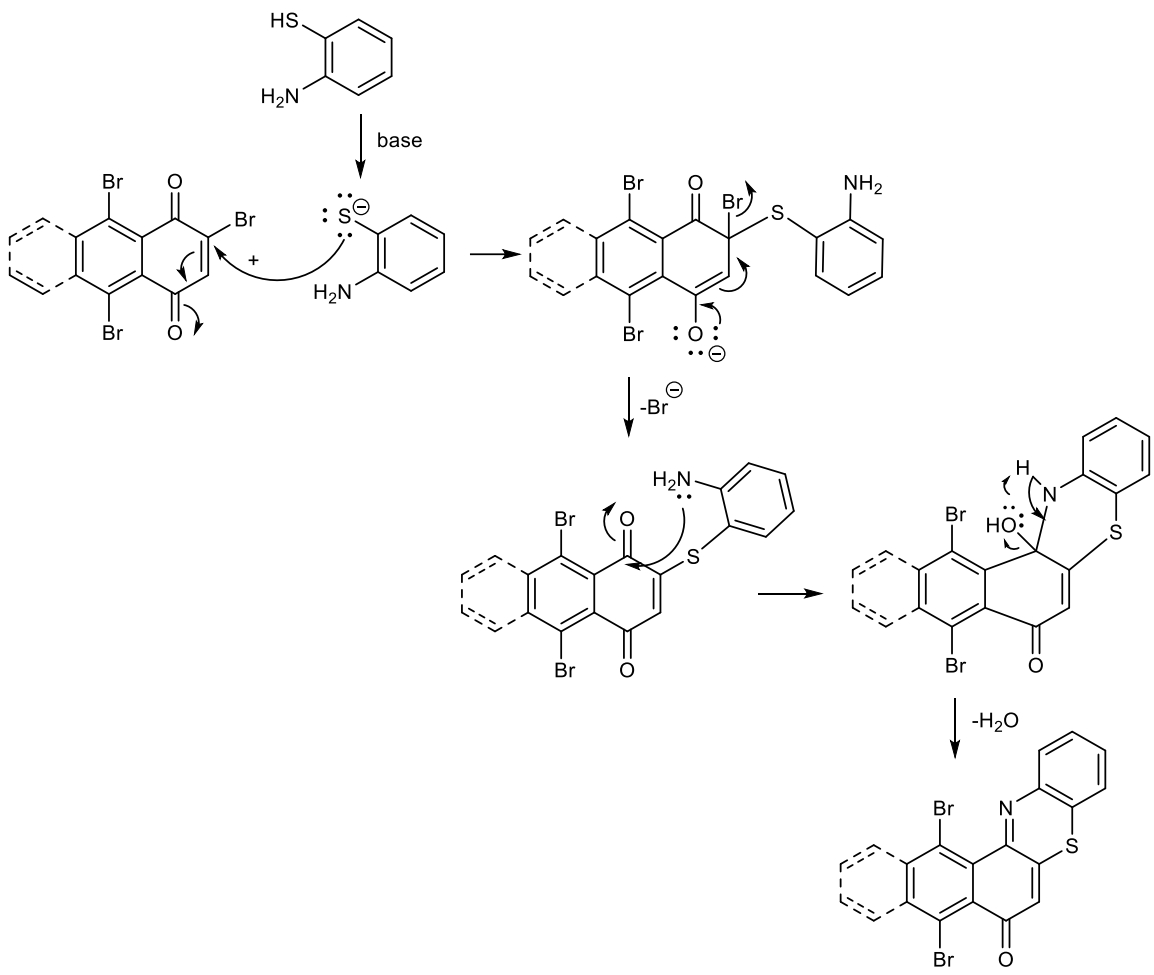

Fig. 3: The reaction mechanism for the formation of the **3** and **4**.

Fingermark Detection

The results of the fresh (one-day) latent fingermark development using phenothiazines **3** and **4** on copier paper have been presented in Fig. 4. Only the first depletion of the depletion series was given for all fingermark test results. Fingermarks developed with compounds **3** or **4** were found to produce a strong photoluminescence when viewed through red filter (cut-off at 590 nm) and when illuminated at 415-515 nm. The best results were obtained at the wavelength at 440 nm.

Positive controls (developed amino acid spots) also exhibited strong photoluminescence (Figure S11), while the negative controls (no fingermark) didn't yield any enhancement. In addition, compound **4** did not cause coloration of the background, while compound **3** resulted in a pale pink coloration of the background.

Transition metal-assisted coupling reactions of α-amino acids with brombenzene derivatives are known [38]. In addition to α-amino acids, the natural fingermark secretions also contain transition metals such as copper (42.5 ng/cm^2), and nickel (36.3 ng/cm^2) [6]. Similar to the reaction suggested by Plater and Harrison [25], the bromo phenothiazines can undergo a coupling reaction with fingermarks containing α-amino acids and transition metals. High temperature can accelerate this reaction. As a second possibility, as in the mechanism proposed for lawsone, the carbonyl group could react with an α-amino acid. The coupling product formed as a result of further reaction with a second phenothiazine compound may exhibit photoluminescent properties [15].

The developed fingermarks were evaluated in terms of sensitivity of the compounds, clarity of the ridges and contrast between background and ridges. It can be indicated when the results obtained with one-day fingermarks were examined that similar results

have been obtained with both compounds in terms of clarity of the ridges and contrast between background and ridges (Figure 4). Papillary lines were quite distinctive. Although there was no significant difference between the two compounds, it can be said that the best average improvement score (score 3.2) has been obtained with compound **4** (Figure 5).

Figure 6 displays the images of developed aged latent fingermarks. Fingermarks were aged for four different times periods (one-week, one-month, three-months, and six-months). The same average improvement scores (scores: 2.4 for three-months, 0 for six-month) were obtained for both compounds for the three- and six-months aging periods (Figure 7). It can be indicated that compound **4** shows a higher improvement average score (score: 2.6) for one-month aging period while compound **3** shows a higher improvement average score (score: 3) for one-week aging period (Figure 7). No improvement could be detected for both compounds during the tests performed using six-months aged fingermarks.

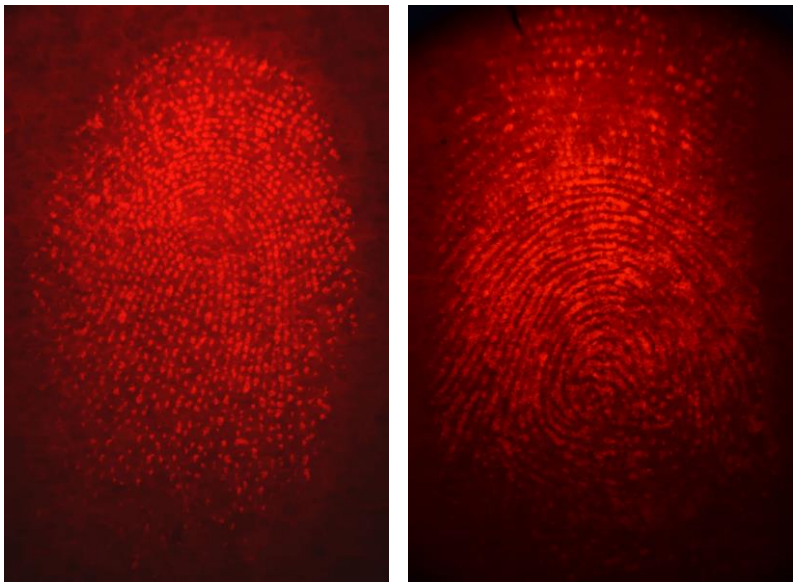

Fig. 4: Latent fingermarks (one-day) developed with phenothiazines **3** (a) and **4** (b).

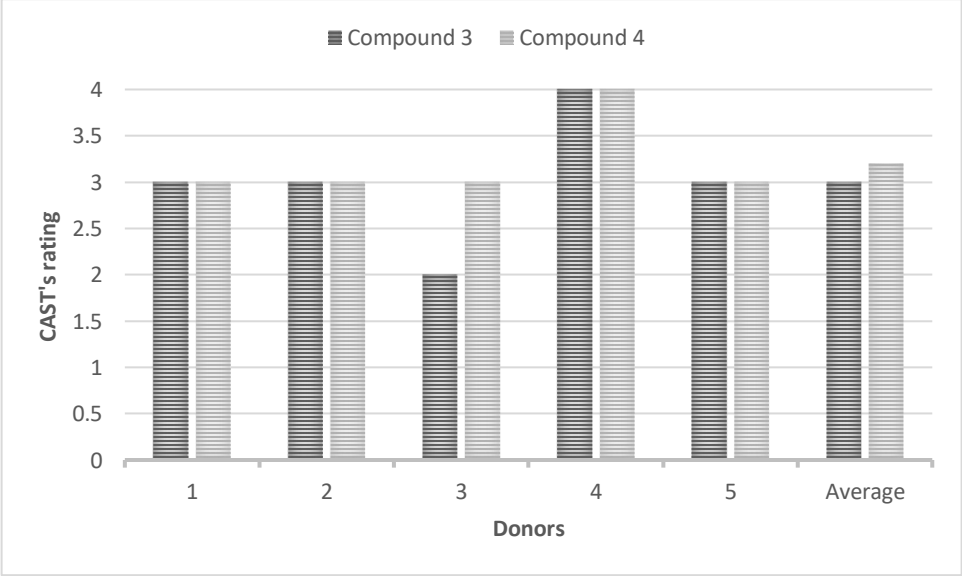

Fig. 5: Development quality (CAST's rating) for phenothiazines **3** and **4**.

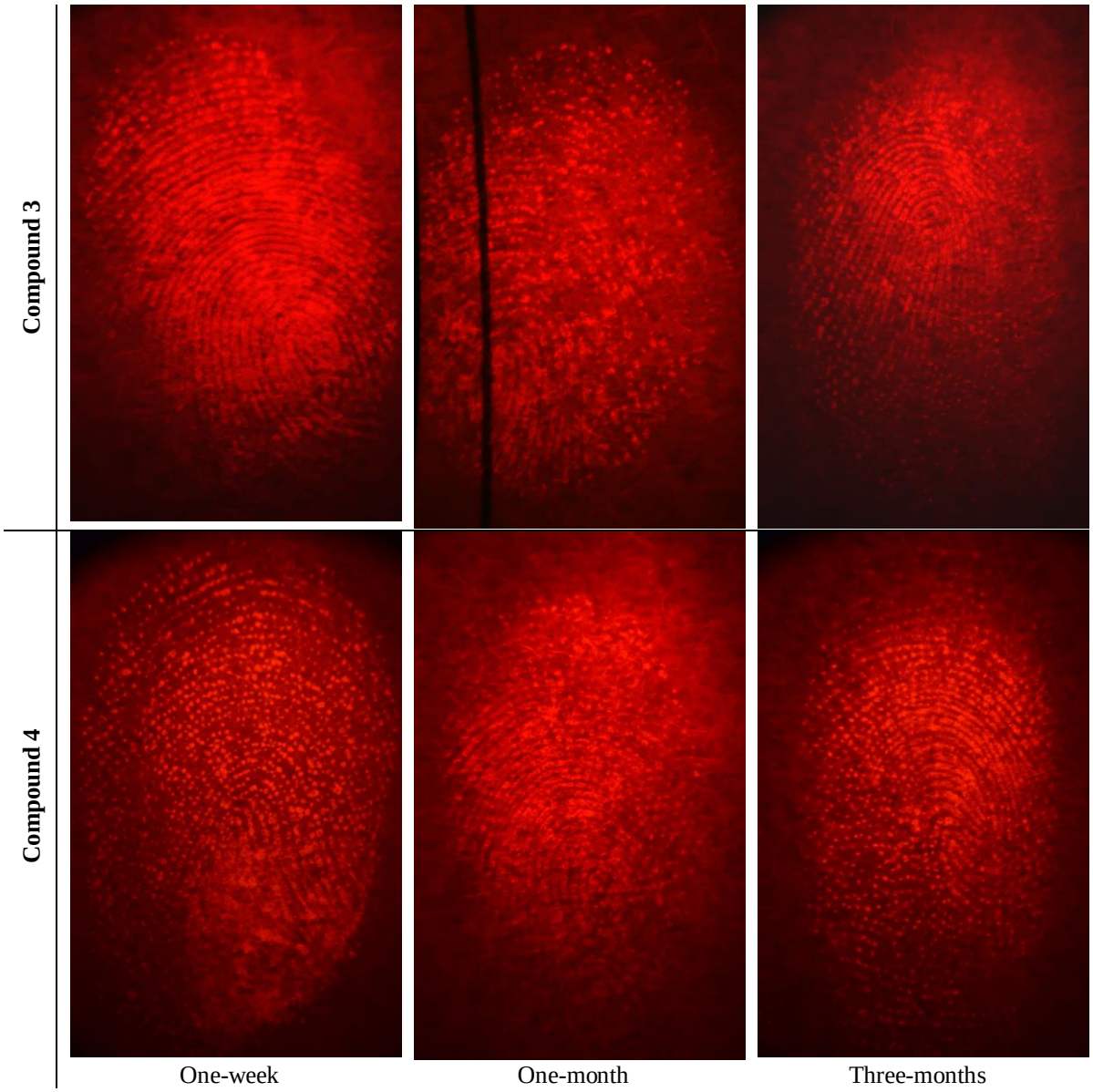

Fig. 6: Aged latent fingermarks developed with phenothiazines **3** and **4**.

*Comparison of Phenothiazines (**3** and **4**) with DFO*

Figure 8 presents examples of latent fingermarks developed with DFO (left side) and phenothiazines **3** and **4** (right side). It can be said that phenothiazines **3** and **4** showed weaker photoluminescence intensity compared with DFO. DFO showed better development compared to compounds **3** and **4** and exhibited greater ridge detail (Figs. 8 and 9). Scores ranged from 0 to -2. Average improvement scores for comparison with DFO for phenothiazines **3** and **4** were -1.2 and -1, respectively (Figure 9).

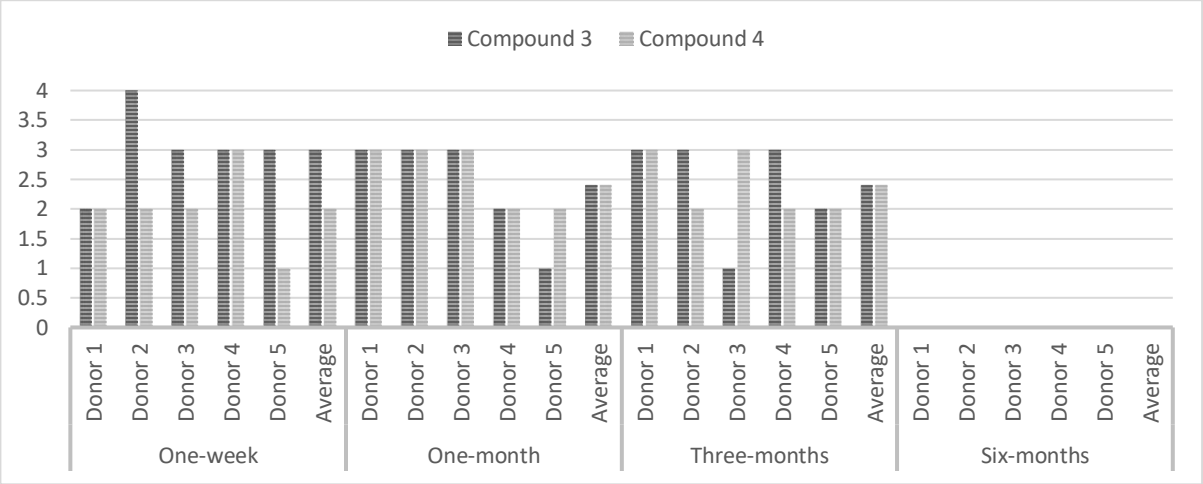

Fig. 7: Development quality (CAST's rating) for aged latent fingermarks developed with phenothiazines **3** and **4**.

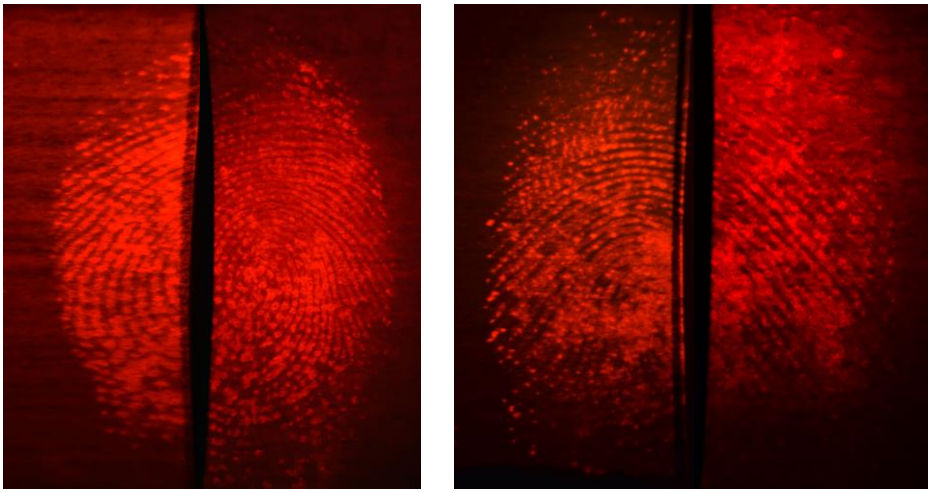

Fig. 8: Comparison between development of latent fingermarks (one-day) with DFO (left) and phenothiazines **3** (a) and **4** (b) (right).

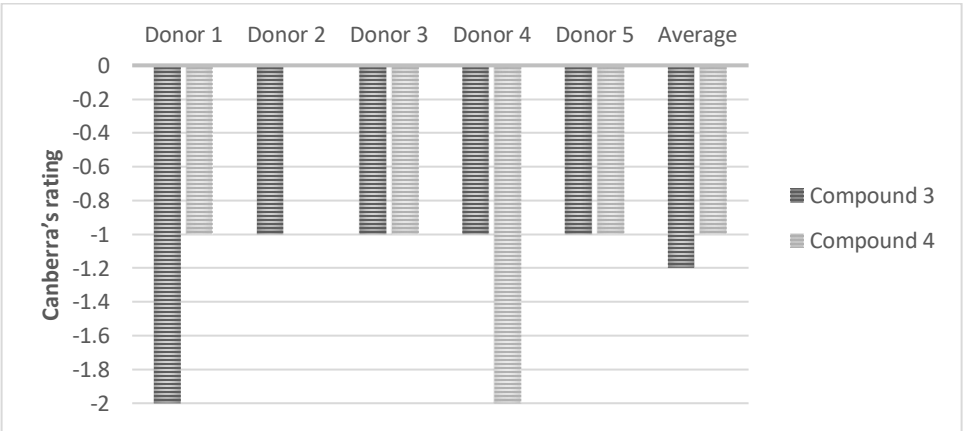

Fig. 9: Development quality (Canberra's rating) for phenothiazines **3** and **4**.

Conclusion

In summary, two new phenothiazines (**3** and **4**) have been synthesized and their usability as fingermark reagents on paper surfaces in criminal investigations have been investigated in comparison with DFO which is one of the commonly used fingermark reagents. The obtained results revealed that the phenothiazines (**3** and **4**) reacted with amino acids in the fingermark secretion on the copier paper to yield photoluminescent prints. The latent fingermarks developed with both compounds have similar performance in terms of sensitivity of the compounds, clarity of the ridges and contrast between background and ridges.

In addition, aged fingermarks, from one-week to six-months were also tested with phenothiazines (**3** and **4**). The results showed that both compounds were also effective even in developing three-month aged fingermarks. A comparison of the phenothiazines and DFO to develop latent fingermarks on copier paper also gave optimistic results. Although phenothiazines (**3** and **4**) showed weaker photoluminescence intensity compared with DFO, it can be stated that certain improvement scores are the same as those for DFO.

In conclusion, preliminary studies indicate that both phenothiazines have a potential to be used as effective reagents for detecting latent fingermarks. Further research is required to investigate the mechanism of the reaction of these compounds with amino acids and determine the structure of the compounds responsible for photoluminescence.

Acknowledgements

This work was supported by the Scientific and Technological Research Council of Türkiye (TUBITAK, Grant No: 115Z880).

References

1. X. Jin, R. Xin, S. Wang, W. Yin, T. Xu, Y. Jiang, X. Ji, L. Chen, J. Liu, A tetraphenylethene-based dye for latent fingerprint analysis, *Sens. and Actuators B Chem.*, **244**, 777 (2017).
2. J.D. De Alcaraz-Fossoul, C.M. Patris, A.B. Muntaner, C.B. Feixat, M.G. Badia, Determination of latent fingerprint degradation patterns-a real fieldwork study, *Int. J. Legal Med.,* **127**, 857 (2013).
3. R. Jelly, S.W. Lewis, C. Lennard, K.F. Lim, J. Almog, Substituted naphthoquinones as novel amino acid sensitive reagents for the detection of latent fingermarks on paper surfaces, *Talanta,* **82**, 1717 (2010).
4. C. Champod, C. Lennard, P. Margot, M. Stoilovic, *Fingerprints and other ridge skin impressions (2nd ed.)*, Boca Raton, FL: CRCPress. p. 120 (2016).
5. S. Cadd, M. Islam, P. Manson, S. Bleay, Fingerrint composition and aging: A literature review, *Science & Justice*, **55**, 219 (2015).
6. R.E. Boseley, B.N. Dorakumbura, D.L. Howard, M. de Jonge, M.J. Tobin, J. Vongsvivut, T.T.M. Ho, W. van Bronswijk, M.J. Hackett, S.W. Lewis, Revealing the elemental distribution within latent fingermarks using synchrotron sourced x-ray fluorescence microscopy, *Anal. Chem.*, **91**, 10622 (2019).
7. F.K. Kanodarwala, S. Moret, X. Spindler, C. Lennard, C. Roux, Nanoparticles used for fingermark detection-A comprehensive review, *WIREs Forensic Sci*., **1**, 1341 (2019).
8. R. Jelly, E.L.T. Patton, C. Lennard, S.W. Lewis, K.F. Lim, The detection of latent fingermarks on porous surfaces using amino acid sensitive reagents: A review, *Anal. Chim. Acta*, 652 128 (2009).
9. J. Gaspar, Z. Nemethova, H. Janekova, A. Gaplovky, H. Stankovicova, Amino acid-sensitive reagents with coumarin moiety for latent prints examination, *Monatsh. Chem.*, **149**, 1787 (2018).
10. K. Berkil Akar, Novel O-propyl, S-propyl, and N-propyl substituted 1,4-naphthoquinones and 1,4-anthraquinones as potential fingermark development reagents for porous surfaces, *J. Forensic Sci.*, **66**, 161 (2021).
11. E.L.T. Patton, D.H. Brown, S.W. Lewis, Detection of latent fingermarks on thermal printer paper by dry contact with 1,2-indandione, *Anal. Methods*, **2**, 631 (2010).
12. C.A. Pounds, R. Grigg, T. Mongkolaussavaratana, The use of 1,8-diazafluoren-9-one (DFO) for the fluorescent detection of latent fingermarks on paper, a preliminary evaluation, *J. Forensic Sci.*, **35**, 169 (1990).
13. R.R. Hark, D.B.Hauze, O. Petrovskaia, M.M. Joullie, Synthetic studies of novel ninhydrin analogs, *Can. J. Chem.*, **79**, 1 (2001).
14. D.B. Hansen, M.M. Joullie, The development of novel ninhydrin analogues, *Chem. Soc. Rev.*, **34**, 408 (2005).
15. R. Jelly, S.W. Lewis, C. Lennard, K.F. Lim, J. Almog, Lawsone: a novel reagent for the detection of latent fingermarks on paper surfaces, *Chem. Commun.*, **30**, 3513 (2008).
16. P. Ravichandiran, S.A. Subramaniyan, A.P. Bella, P.M. Johanson, A.R. Kim, K.S. Shim, D.J. Yoo, Simple Fluorescence Turn-on chemosensor for

selective detection of Ba^{2+} ion and its live cell imaging, *Anal. Chem.*, **91**, 10095 (2019).
17. P. Ravichandiran, D.S. Prabakaran, A.P. Bella, A. Boguszewska-Czubara, M. Maslyk, K. Dineshkumari, P.M. Johnson, B.-Y. Park, M.-K. Han, H.G. Kim, D.J. Yoo, Naphthoquinone-dopamine linked colorimetric and fluorescence chemosensor for selective detection of Sn^{2+} ion in aqueous medium and its bio-imaging applications, *ACS Sustainable Chem. Eng.*, **8**, 10947 (2020).
18. P. Ravichandiran, D.S. Prabakaran, N. Maroli, A. Boguszewska-Czubara, M. Maslyk, A.R. Kim, P. Kolandaivel, P. Ramalingam, B.-H. Park, M.-K. Han, T. Ramesh, D.J. Yoo, Mitochondria-targeted dual-channel colorimetric and fluorescence chemosensor for detection of Sn^{2+} ions in aqueous solution based on aggregation-induced emission and its bioimaging applications, *J. Hazard. Mater.*, **415**, 125593 (2021).
19. P. Ravichandiran, A. Boguszewska-Czubara, M. Maslyk, A.P. Bella, P.M. Johnson, S.A. Subramaniyan, K.S. Shim, D.J. Yoo, A phenoxazine-based fluorescent chemosensor for dual channel detection of Cd^{2+} and CN^{-} ions and its application to bio-imaging in live cells and zebrafish, *Dyes Pigm.*,**172**, 107828 (2020).
20. J. Chan, Ph.D. Thesis, *Synthesis, characterisation and application of novel quinones for the detection of latent fingermarks*, University of Technology Sydney (UTS), (2019).
21. K. Berkil Akar, Evaluation of alizarin and purpurin dyes for their ability to visualize latent fingermark on porous surfaces, *Science & Justice*, **61**, 130 (2021).
22. P. Ravichandiran, J. Athinarayanan, D. Premnath, V.S. Periasamy, A.A. Alshatwi, S. Vasanthkumar, Synthesis, molecular docking and biological evaluation of novel 6-(4-(4-aminophenylsulfony)phenylamino-5H-benzo[a]phenothiazin-5-one derivatives, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc*., **139**, 477 (2015).
23. F.N. Ibeanu, E.A. Onoabedje, A. Ibezim, U.C. Okoro, Synthesis, characterization, computational and biological study of novel azabenzo[a]phenothiazine and azabenzo[b]phenoxazine heterocycles as potential antibiotic agent, *Med. Chem. Res.*, **27**, 1093 (2018).
24. J.F. Fischer. *A preliminary study of phenothiazine derivatives used in conjunction with argon ion laser excitation for the detection of latent prints.* The International Forensic Symposium on Latent Prints. 133.
25. M.J. Plater, W.T. Harrison. Characterisation of 3, 7-dibromophenothiazin-5-ium perbromide and its use for enhancing latent fingerprints. *J. Chem. Res.*, **6**, 384 (2009).
26. K.J. Day, W. Bowker, Enhancement of cyanoacrylate developed latent prints using Nile Red. *J. Forensic Ident*., **46**, 183 (1996).
27. K. Braasch, M. de la Hunty, J. Deppe, X. Spindler, A.A. Cantu, P. Maynard, C. Lennard, C. Roux, Nile red: Alternative to physical developer for the detection of latent fingermarks on wet porous surfaces?, *Forensic Sci. Int.*, **230**, 74 (2013).
28. A.A. Frick, F. Busetti, A. Cross, S.W. Lewis, Aqueous Nile blue: A simple, versatile and safe reagent for the detection of latent fingermarks. *Chem. Commun*., **50**, 3341 (2014).
29. W. Wang, J. Xing, Z. Ge, Evaluation of Nile Red-Loaded Mesoporous Silica Nanoparticles for Developing WaterSoaked Fingerprints on Thermal Paper, *J. Forensic Sci.*, **64**, 717 (2019).
30. C. Didierjean, M. Debart, F. Crispino. New Formulation of DFO in HFE-7100. *Fingerprint World*, **24**, 163 (1998).
31. L.W.L. Davis, Ph.D. Thesis, *Novel techniques for the development of latent fingermarks*. Loughborough, U.K.: Loughborough University, (2017).
32. N. Attard-Montalto, J.J. Ojeda, A. Reynolds, M. Ismail, M. Bailey, L. Doodkorte, M. de Puit, B.J. Jones, Determining the chronology of deposition of natural fingermarks and inks on paper using secondary ion mass spectrometry. *Analyst.*, **139**, (2014) 4641-4654.
33. International Fingerprint Research Group (IFRG). Guidelines for the assessment of fingermark detection techniques, *J. Forensic Identif.*, **64**, 174 (2014).
34. C. McLaren, C. Lennard, M. Stoilovic, Methylamine pretreatment of dry latent fingermarks on polyethylene for enhanced detection by cyanoacrylate fuming. *J. Forensic Identif.*, **60**, 199 (2010).
35. O. Çakmak, K. Berkil Akar, N. Kaplan. Functionalization of naphthalene: a novel synthetic route to brominated naphthoquinones. *Arkivoc*, **vii**, 274 (2012).
36. K. Berkil Akar, O. Çakmak, E. Şahin. Synthesis and characterization of a novel conformation of 2,9,10-tribromoanthracene-1,4-dione. *J. Chem. Crystallogr.*, **43**, 677 (2013).
37. J.Z. Davalos, P. Jimenez, M.V. Roux, M.T. Molina, T. Filipova, E. Lewars, J.F. Liebman, Thermochemical and structural properties of anthraquinones, *Struct. Chem.*, 24, 2027 (2013).
38. D. Ma, Q. Cai, Copper/amino acid catalyzed cross-couplings of aryl and vinyl halides with nucleophiles. *Acc. Chem. Res.*, **41**, 1450 (2008).