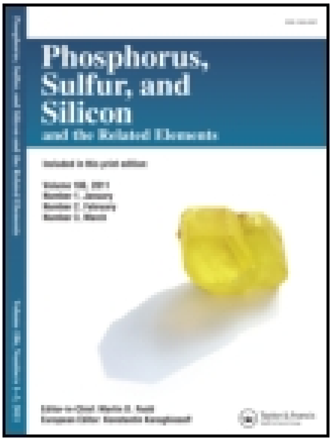

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# Synthesis and Absorption Properties of Some 4-Mercapto-1,8-naphthalimides, 4-Mercapto-7H-benzimidazo[2,1-a]benz[d,e] Isoquinolin-7-one, and 4-Mercapto-7H-benzimidazo [2,1-a]Benz[d, e]isoquinoline-7-one

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# Synthesis and Absorption Properties of Some 4-Mercapto-1,8-naphthalimides, 4-Mercapto-7*H*-benzimidazo[2,1-*a*]benz[*d,e*] Isoquinolin-7-one, and 4-Mercapto-7*H*-benzimidazo [2,1-*a*]Benz[*d, e*]isoquinoline-7-one

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*The reaction of 4-chloro-1,8-naphthalic anhydride with sulfur and sodium sulfide in boiling ethanol lead to 4-mercapto-1,8-naphthalic anhydride. The condensation of a later compound with amines produced 4-mercapto-1,8-naphthalimides and with ethylenediamine and orthophenylenediamine, respectively, led to 4-mercapto-7H-imidazo[2,1-a]benz[d,e]isoquinoline-7-one and 4-mercapto-7H-imidazo[2,1-a]benz[d,e]isoquinoline-7-one in good to fairly high yields.*

**Keywords** 4-Chloro-1,8-naphthalic anhydrides; 4-mercapto-1,8-naphthalimides; ethylendiamine; orthophenylendiamine

## INTRODUCTION

4-substituted-1,8-naphthalimide derivatives have scientific interest because of their potential use as polymerizable fluorophores for synthetic polymers,[1–6] fluorescent dyes for solar energy collectors,[7] organic light emitting diodes,[8] markers in molecular biology,[9] in laser active media,[10,11] in medicine as antitumors,[12] and as an analgesic.[13] Recently, some 3-brominated-1,8-naphthalimides have been proposed for the photoinactivation of HIV.[14] In this study, we report the synthesis of fluorophores that have a mercapto group at the $C_4$ position in the 1,8-naphthalimide structure, and their absorption properties are also investigated.

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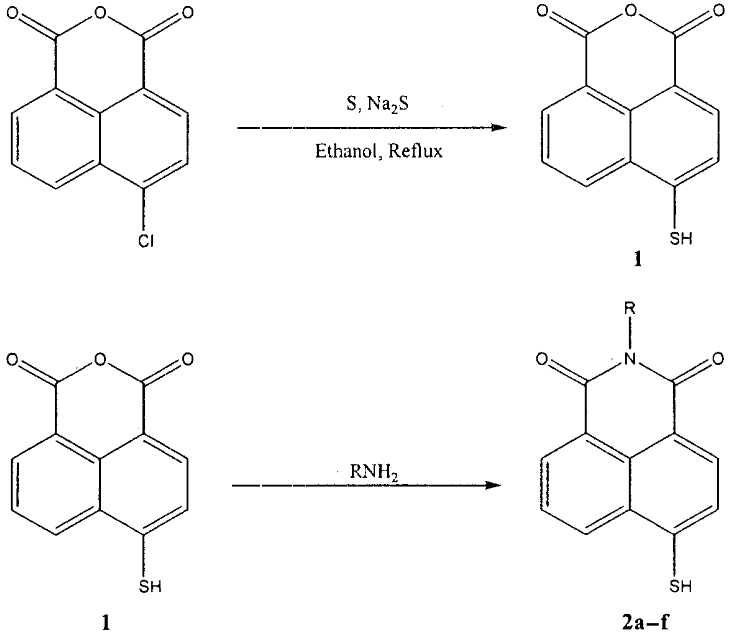
## RESULTS AND DISCUSSION

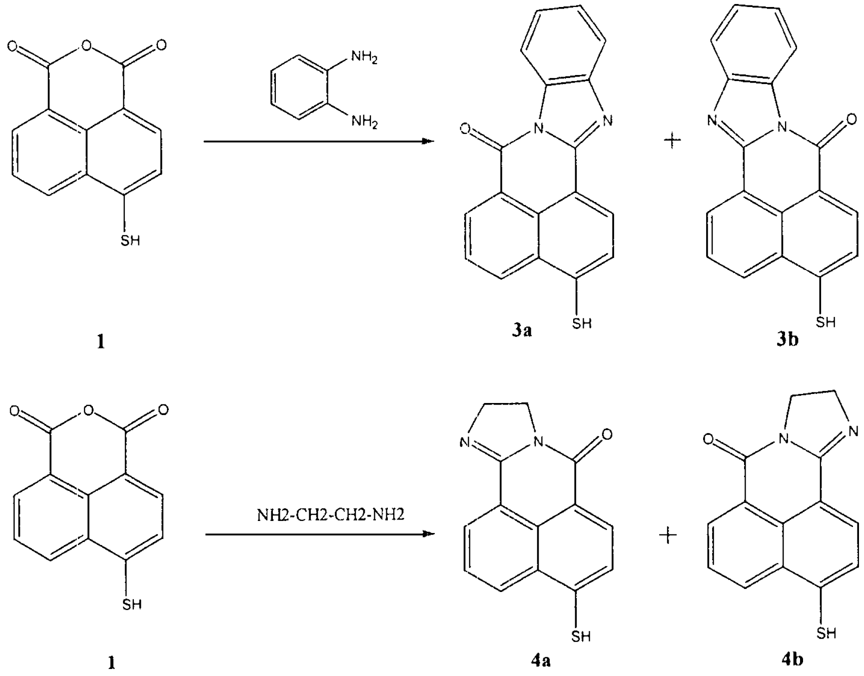
The synthetic route for obtaining the final products is presented in Schemes 1 and 2. The 4-chloro-1,8-naphthalic anhydride have been used as conventional starting material for the preparation of mercaptoimides. 4-mercapto-1,8-naphthalic anhydride were synthesized by an indicated procedure.[15] This compound shows a 38-nm bathochromic displacement compared with 4-chloronapthalic anhydride; this phenomenon is for better resonance and a strong conjugated system, because the thiol group is a better electron donor than a chlorine atom. This compound has good color and fluorescent properties. 4-chloronaphthalic anhydride is a pale yellow solid and 4-mercaptonaphthalic anhydride is yellow. Spectroscopic data and physical properties of 4-mercaptonaphthalimides and 4-mercapto-7H-imidazo[2,1-a]benz[d,e]isoquinoline-7-one and 4-mercapto-7H-benzimidazo[2,1-a]benz[d,e]isoquinoline-7-one are summarized in Tables I and II.

## EXPERIMENTAL

Melting points were determined with an electrothermal 9100 apparatus and are uncorrected. The infrared spectra were recorded on a



**SCHEME 1**



SCHEME 2

**TABLE I Spectroscopic Data and Physical Properties of 4-Mercapto-1,8-Naphthalimide Derivatives**

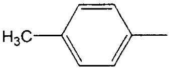
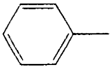
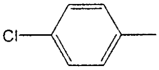
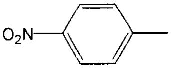
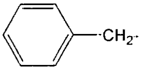
| Compound | R | (%) | M.P. | $\lambda_{max}$ |
|---|---|---|---|---|
| **2a** | $CH_3CH_2CH_2$- | 87 | 220–223 | 374.4 |
| **2b** |  | 77 | 260–262 | 374.4 |
| **2c** |  | 92 | 260–263 | 376 |
| **2d** |  | 78 | 258–260 | 377.5 |
| **2e** |  | 78 | 261–263 | 370.9 |
| **2f** |  | 81 | 220–222 | 382.4 |

**TABLE II Spectroscopic Data and Physical Properties of 3a, 3b, 4a, and 4b**

| Compound | MP/°C | (%) | $\lambda_{max}$ | Color |
|---|---|---|---|---|
| **2a, 3b** | 258–260 | 92 | 414.4 | Orange |
| **4a, 4b** | 203–205 | 63 | 435.2 | Orange |

Philips PU 9800 FT-IR spectroscopy. UV spectra were obtained on a UNICAM 8700 series UV/Vis spectrometer, Mass Spectra were recorded on a Finnigan-Malt 8430 Mass spectrometer operating at an ionization potential of 70 eV. Elemental analysis were performed using a Heraeus CHN-O-Rapid analyzer. The chemicals were obtained from Fluka (Buchs, Switzerland) and Merck and were used without further purification.

## General Procedure

### *Synthesis of 4-Mercapto-1,8-naphthalic anhydride*

4.65 g (20 mmol) of 4-chloro-1,8-naphthalic anhydride, 2.12 g of sulfur, and 6 g (60 mmol) of sodium sulfide were poured into 50 mL of ethanol, and the mixture was refluxed for 3 h. At the end of reaction, the cooled, deep red liquid was added to 200 mL of water; the solution was acidified with glacial acetic acid. A yellow solution was obtained, which was added to 125 mL of 1% NaOH solution. The surplus sulfur was separated and the filtered solution was acidified with glacial acetic acid. A yellow solid was obtained. The mixture was filtered and the crude product was recrystallized with chlorobenzene. $\upsilon_{max}$ (KBr): 2350 cm$^{-1}$(SH),1750–1785 cm$^{-1}$ (two carbonyl groups),
M.p.: 280–282°C; Yield: 63%, $C_{12}H_6O_3S$: (MW:230).

### *The Typical Procedure for the Preparation of 2a–f in Table I*

0.02 g (0.1 mmol) of 4-mercapto-1,8-naphthalic anhydride with 0.04 g (0.3 mmol) of 4-chloroaniline and 5 mL of glacial acetic acid were refluxed for 1 h. At the end, the solution was added to 10 mL of distilled water; a yellow precipitate was obtained; the mixture was filtered, and the crude product was crystallized with toluene.

### *The Typical Process for the Preparation of 3a, 3b, 4a, and 4b in Table II*

0.02 g (0.1 mmol) of 4-mercapto-1,8-naphthalic anhydride, 0.02 g (0.2 mmol) of *ortho*-phenylenediamine, and 5 mL of glacial acetic acid were refluxed for 1.5 h. At the end, the solution was added to 10 mL of distilled water; an orange precipitate was obtained. The mixture was filtered, and the crude product was crystallized with DMF.

2a: $C_{15}H_{13}NO_2S$: (MW: 271), elemental analysis: Calc.: C: 66.42; H: 4.79; N: 5.16; O: 11.88. Found: C, 66.11; H: 4.81; N: 5.05, O: 11.94.
$\upsilon_{max}$ (KBr): 1690, 1649 $cm^{-1}$ (imide carbonyls), 1378$cm^{-1}$ C—N.

2b: $C_{19}H_{13}NO_2S$: (MW: 319), Elemental analysis: Calc.: C: 71.47; H: 4.07; N: 4.38; O: 10.03; S: 10.03. Found: C: 71.25; H: 4.08; N: 4.29; O: 10.13; S: 10.05.
$\upsilon_{max}$ (KBr): 1763 $cm^{-1}$, 1723 $cm^{-1}$ (imide carbonyls) C—N: 1323 $cm^{-1}$.

2c: $C_{19}H_{13}NO_2S$: (MW: 305), Elemental analysis: Calc.: C: 70.81; H: 3.60; N: 4.59; O: 10.49; S: 10.49. Found: C: 71.02; H: 3.62; N: 4.51; O: 10.62; S: 10.48.
$\upsilon_{max}$ (KBr): 1762, 1725 (imide carbonyls) C—N: 1323 $cm^{-1}$.

2d: $C_{18}H_{10}NO_2SCl$: (MW: 339.5), Elemental analysis: Calc.: C: 63.62; H: 2.94; N: 4.12; O: 9.42; S: 9.42; Cl: 10.45. Found: C: 63.65; H: 2.98; N: 4.07; O: 9.53.
$\upsilon_{max}$ (KBr): 1764, 1725 (imide carbonyls), 1334 $cm^{-1}$.

2e: $C_{18}H_{10}N_2O_4S$: (MW: 350), Elemental analysis; Calc: C: 61.71, H: 2.85, N: 8.00, O: 18.28, S: 9.14. Found: C: 61.64, H: 2.89, N: 8.02, O: 18.34, S: 9.23
$\upsilon_{max}$ (KBr): 1762, 1723 $cm^{-1}$ (imide carbonyls), 1550, 1323 $cm^{-1}$, $NO_2$

2f: $C_{19}H_{13}NO_2S$: (MW: 319), Elemental analysis; Calc: C: 71.47, H: 4.07, N: 4.38, O: 10.03, S: 10.03. Found: C: 71.33, H: 4.02, N: 4.43, O: 10.09, S: 10.12
$\upsilon_{max}$ (KBr): 1689, 1648 $cm^{-1}$, (imide carbonyls), 1379 $cm^{-1}$ C—N

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