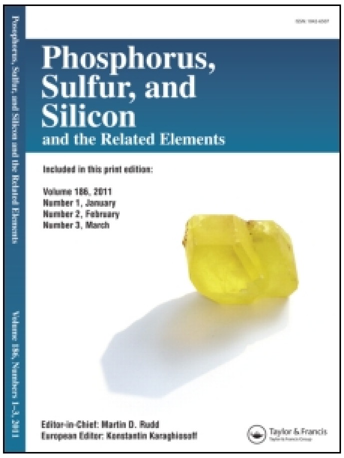

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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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To cite this Article Hekmatshoar, R. , Beheshtiha, S. Y. S. , Nazari, A. and Faridbod, F.(2006) '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', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 7, 1521 — 1526

To link to this Article: DOI: 10.1080/10426500500269497

URL: http://dx.doi.org/10.1080/10426500500269497

Phosphorus, Sulfur, and Silicon, 181:1521–1526, 2006
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500269497

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.

Received April 12, 2005; accepted May 10, 2005.

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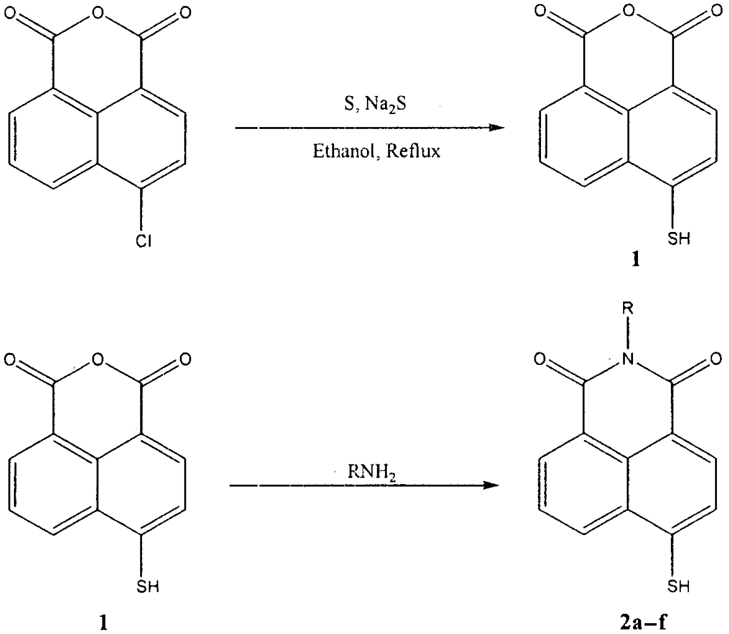
RESULTS AND DISCUSSION

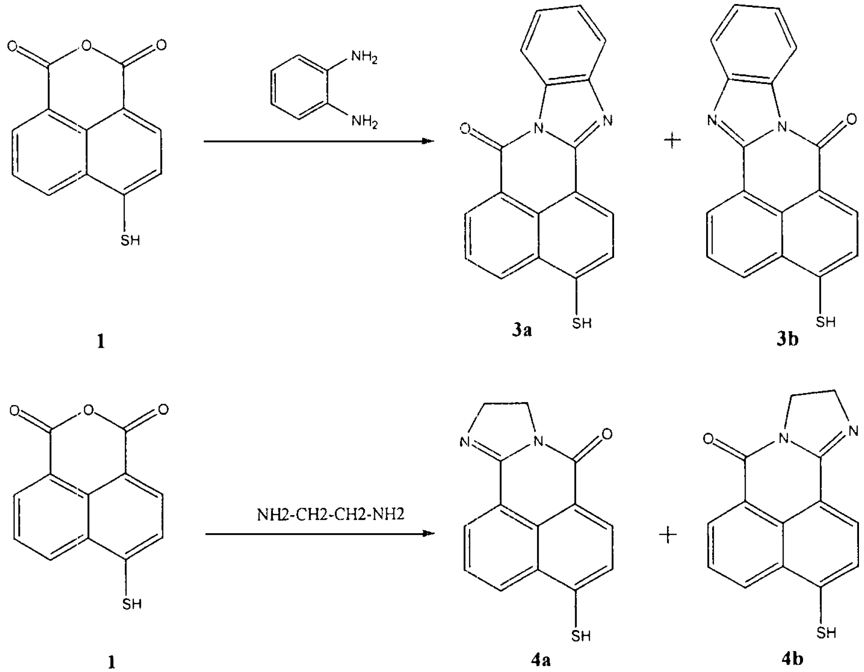
The synthetic route for obtaining the final products is presented in Schemes 1 and 2. The 4-chloro-1,8-naphthalic anhydride have been used as conventional starting material for the preparation of mercaptoimides. 4-mercapto-1,8-naphthalic anhydride were synthesized by an indicated procedure.[15] This 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

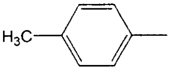
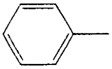
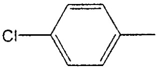
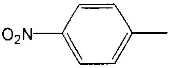
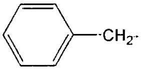
Compound	R	(%)	M.P.	λ_{max}
2a	$CH_3CH_2CH_2$-	87	220–223	374.4
2b		77	260–262	374.4
2c		92	260–263	376
2d		78	258–260	377.5
2e		78	261–263	370.9
2f		81	220–222	382.4

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

Compound	MP/°C	(%)	λ_{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. υ_{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.
υ_{max} (KBr): 1690, 1649 cm^{-1} (imide carbonyls), 1378cm^{-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.
υ_{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.
υ_{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.
υ_{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
υ_{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
υ_{max} (KBr): 1689, 1648 cm^{-1}, (imide carbonyls), 1379 cm^{-1} C—N

REFERENCES

[1] T. Konstantinova, P. Meallier, and I. Grabcher, *Dyes and Pigments*, **22,** 191 (1993).
[2] I. Grabchev, T. Konstantinova, P. Mealier, and M. Popova, *Dyes and Pigments*, **28,** 41 (1995).
[3] T. Konstantinova, and I. Grabchev, *J. App/Polym Sci.*, **62,** 447 (1996).
[4] T. Filipova, I. Grabchev, and I. Petkov, *J. polym. Sci. Chem.*, **35,** 1069 (1997).
[5] I. Grabchev and T. Philipova, *Dyes and Pigments*, **27,** 321 (1995).
[6] T. Konstantinova and I. Grabchev, *Polym. In.*, **43,** 39(1997).
[7] X. Qian, K. Zhu, and K. Chen, *Dyes and Pigments*, **11,** 13 (1989).
[8] R. Cacialli, E. Friend, C. M. Bouche, P. Le Barni, H. Facoetti, F. Sayer, and P. Robin, *J. App/Phys.*, **83,** 2343.
[9] K. Dubey, R. Singh, and K. Mizra, *Indian J. Chem.*, **34B,** 876 (1995).
[10] E. Martin, R. Weigand, and A. Pardo, *J. Lumines*, **68,** 157 (1996).

[11] V. Gruzinski, A. Kukhta, and G. Shakkah, *J. App / Spectr*, **65,** 444 (1998).
[12] R. Middleton, and J. Parrick, *J. Hetero. Chem.*, **22,** 1567 (1985).
[13] A. D. Andricopulo, R. A. Yunes, V. Cechinel Filho, R. Correa, A. W. S. Filho, A. R. Santos, and R. J. Nunes, *Acta Farm Bonaercpes.*, **17,** 219 (1998).
[14] S. C. Chang, B. Archer, R. Utech, D. Levis, M. Judy, and J. Matthews, *Biorganic Med. Chem. Lett.*, **3,** 555 (1993).
[15] A. Tpeters and S.Y.S. Beheshtiha, *J. Chem. Tech. and Biotech.*, 319 (1986).