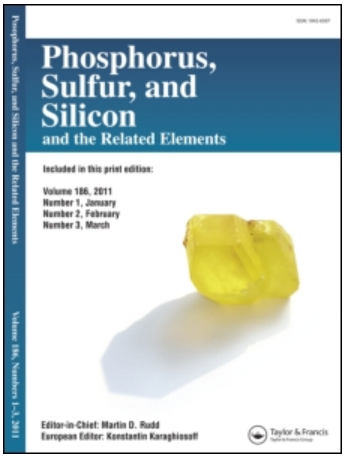

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Online publication date: 16 August 2010

To cite this Article Beheshtiha, S. Y. S. , Hekmatshoar, R. and Soltani, F.(2004) 'SYNTHESIS AND ABSORPTION PROPERTIES OF SOME NEW 4-THIO-1,8-NAPHTHYLIMIDES AND 4-(THIO)-*7H*-BENZIMIDAZO [2,1-A] BENZ [D,E] ISOQUINOLIN-7-ONE DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 9, 1723 — 1729
To link to this Article: DOI: 10.1080/10426500490466328
URL: http://dx.doi.org/10.1080/10426500490466328

Phosphorus, Sulfur, and Silicon, 179:1723–1729, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490466328

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SYNTHESIS AND ABSORPTION PROPERTIES OF SOME NEW 4-THIO-1,8-NAPHTHYLIMIDES AND 4-(THIO)-7*H*-BENZIMIDAZO [2,1-A] BENZ [D,E] ISOQUINOLIN-7-ONE DERIVATIVES

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(Received November 25, 2003; accepted January 6, 2004)

*A series of new 1,8-naphthylimide and 4-(thio)-7*H*-benzimidazo[2,1-a]benz[d,e]isoquinolin-7-one derivatives has been synthesized, and the UV/Vis absorptioin characteristics discussed. Substituents' effect on the UV/Vis absorption characteristics have been investigated.*

Keywords: 1,8-Naphthylimides; 4-(thio)-7*H*-benzimidazo [2,1-a] benz [d,e]isoquinolin-7-one derivatives

INTRODUCTION

During recent years, 4-substituted-1,8-naphthylimide derivatives and 4-substituted-7*H*-benzimidazo[2,1-a]benz[d,e]isoquinolin-7-one derivatives have aroused scientific interest because of their potential use as excellent yellow, orange and red dye stuffs for synthetic fibers[1] and as polymerizable fluorophores for synthetic polymers. A series of fluorescent polymerizable 1,8-naphthylimide[2–6] were synthesized and their ability to polymerize with styrene, methyl methacrylate or acrylonitrile, obtaining copolymers with intensive fluorescence,[7–12] was studied.

Recently, 1,8-naphthylimide dyes have been examined with regards to their use in nematic liquid crystals for guest-host–type electro-optical displays.[13,14] Fluorescent 1,8-naphthylimide derivatives are very interesting in view of their usage as fluorescent dyes, solar energy collectors,[15] organic light-emitting diodes,[16] markers in molecular biology,[17] in laser active media,[18,19] and in medicine as antitumours[20]

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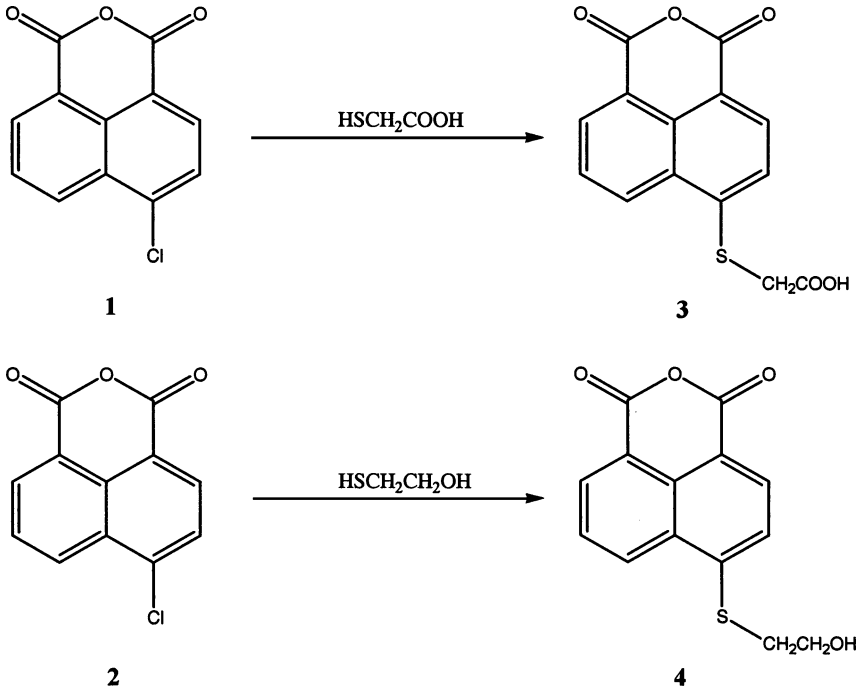
and analgesics.[21] Recently, some 3-brominated compounds of 1,8-naphthylimide have been proposed for the photoinactivation of HIV.[22]

The present work concerns the synthesis of new 1,8-naphthylimides and 4-(thio)-7*H*-benzimidazo [2,1-a] benz [d,e] isoquinolin-7-one derivatives that have different substituents at the C-4 position in the 1,8-naphthalic anhydride structure; some of their absorption properties are also investigated.

RESULT AND DISCUSSIONS

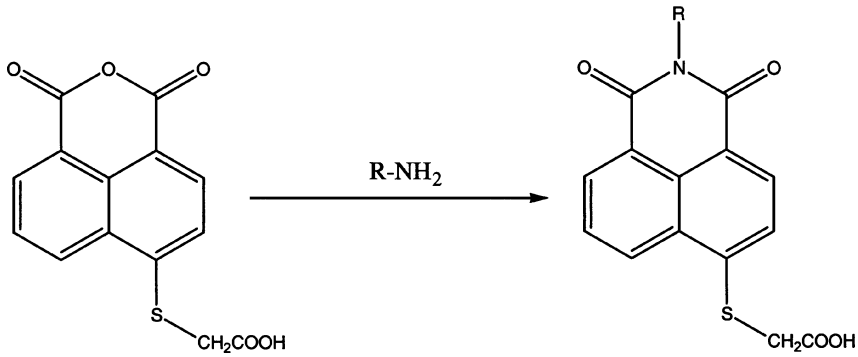
The first step is the synthesis of new thioethers from 4-chloronaphthalic anhydride. This reaction is SN_2, the convenient solvent is DMF or 2-methoxy ethanol, and $NaHCO_3$ as a base is used too. DMF is better than 2-methoxy ethanol but in temperatures higher than 190°C it will decompose. Thiols are highly nucleophilic compounds and other solvents can be used, such as 2-methoxy ethanol, for their reaction with 4-chloronaphthalic anhydride. The ratio of nucleophile to substrate is important. We found that the best ratio according to different



1 3

2 4

SCHEME 1



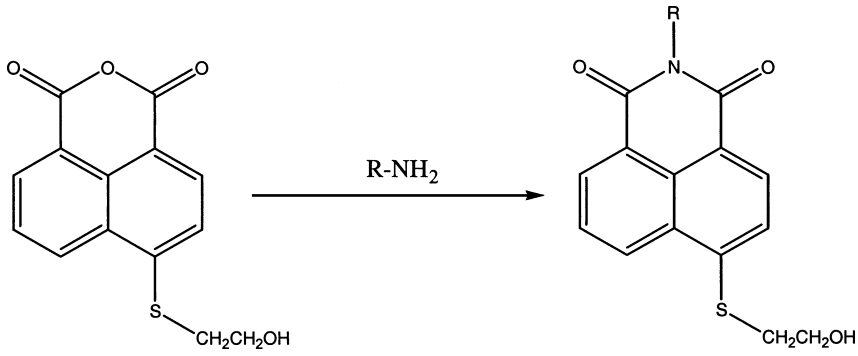
SCHEME 2

concentration of reactions is (Nu/Su = 2/1), and for the determination of the best time of reflux and yields we have used TLC.

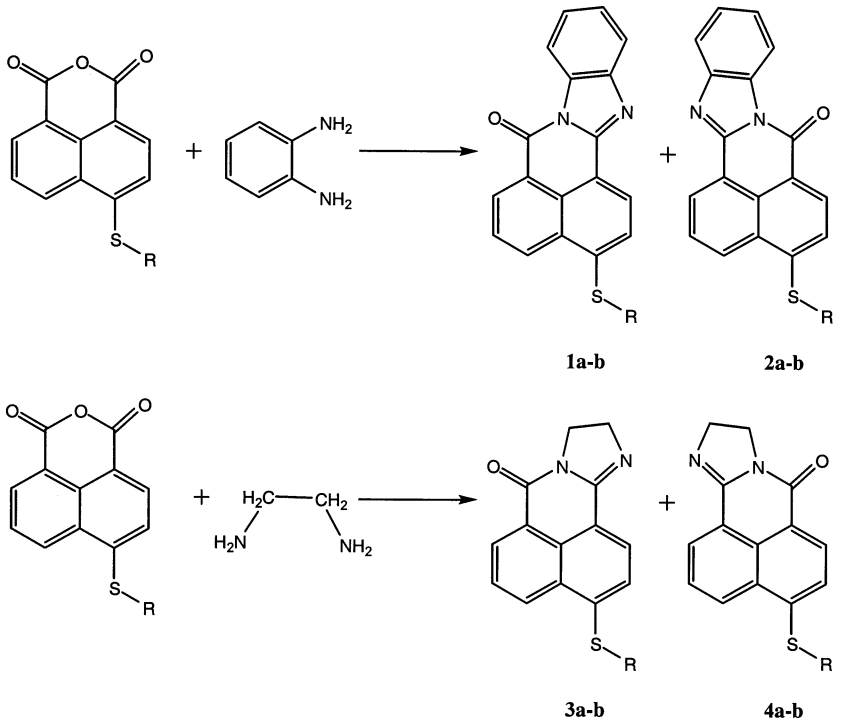
The infrared (IR) and mass spectra of the products clearly indicated the formation of the products.

EXPERIMENTAL

Melting points were determined with an electrothermal 9100 apparatus and are uncorrected. The IR spectra were obtained on Philips pu 9800 Fourier transform infrared (FTIR) spectrometer. Ultraviolet (UV) spectra were recoded on a UNICAM 8700 series UV/Vis spectrometer. 4-chloronaphthalic anhydride was obtained from Alderich and the other chemicals were obtained from Merck and were used without further purification.



SCHEME 3



SCHEME 4

General Procedure

Typical Synthesis of Products (Table I): 4-(Thioacetic acid)-1,8-naphthalic Anhydride

First 2.32 g (10 mmol) of 4-chloronaphtalic anhydride, 2.3 g (20 mmol) of 2-mercaptoacetic acid, and 2.52 g (30 mmol) of sodium bicarbonate were refluxed in 30 ml of DMF for 1 h (progress of the reaction checked by TLC). Then the solution was cooled and acidified with HCl 5% to form

TABLE I Spectroseopic Data and Physical Properties of Naphthalic Anhydride, 4-chloronaphthalic Anhydride, and 4-thio-1,8-naphtalic Anhydride Derivatives

Entry	Compound	λ_{max}(nm)loge	m.p°C	Yield (%)	Color
1	H	330.2	265–267	—	Pale yellow
2	Cl	338.5	216–217	—	White
3	SCH_2COOH	384.2	202	91	Yellow
4	SCH_2CH_2OH	389.3	187	90	Yellow

TABLE II Spectroseopic Data and Physical Properties of 4-thio-1,8-naphthylimides

Entry	R	Mp (°C)	Yield (%)	Color	λ_{max} (nm)
1	$PhCH_2$—	185–186	81	Yellow	386.9
2	p-NO_2-Ph—	227	85	Yellow	390
3	p-CH_3-Ph—	188–189	87	Yellow	385.3
4	p-NH_2-Ph—	175–176	82	Greenish yellow	386.4
5	p-COOH—Ph—	198	78	Bright yellow	386.1
6	p-CH_3-CO—NH—Ph—	197	88	Greenish yellow	388.9

a yellow precipate, which was filtered and recrystallized in ethanol. m.p., 202°C; yield, 91%.

Typical Synthesis of Products (Table I): 4-(Ethanol thio)-1,8-naphthalic Anhydride

First 2.32 g (10 mmol) of 4-chloronaphthalic anhydride, 1.17 g (15 mmol) of 2-mercaptoethanol, and 0.84 g (10 mmol) of sodium hydrogen carbonate in 30 ml of 2-methyoxy ethanol were refluxed for 6 h. The color of the solution was dark brown during the reaction time (the end of the reaction was determined with TLC). The solution was cooled and acidified with HCl 5%; a dark yellow precipate was formed. The crude product was recrystallized in ethanol. m.p., 187°C; yield, 91%. IR (3000 cm^{-1} acidic OH, 2977 cm^{-1} CH aliphatic, 1750, 1770 cm^{-1} anhydride C=O group).

Typical Synthesis of Products (Tables II and III): 4-(Thioacetic acid)-N-benzyl-1,8-naphthylimide

First 0.06 g (0.2 mmol) of 4-(thioacetic acid)naphthalic anhydrid, 1 ml of benzyl amine, and 10 ml of 2-methoxy ethanol were refluxed for 5 h. Then the mixture was poured into 10 ml of distillated water. The solid

TABLE III Spectroseopic Data and Physical Properties of 4-thio-1,8-naphthylimides

Entry	R	Mp (°C)	Yield (%)	Color	λ_{max} (nm)
1	$PhCH_2$—	180–182	86	Yellow	394.8
2	p-NO_2-Ph—	132	62	Yellow	394.8
3	p-CH_3-Ph—	172–173	81	Yellow	394.2
4	p-NH_2-ph—	210	80	Greenish yellow	396.3
5	p-COOH-Ph—	133–134	78	Bright yellow	392.9
6	p-CH_3-CO-NH-Ph—	188	85	Greenish yellow	394.1
7	NH_2—	218–220	87	Pale yellow	399.2

TABLE IV Spectroseopic Data and Physical Properties of 1a–b, 2a–b, 3a–b, 4a–b

Entry	R	Mp (°C)	Yield (%)	Color	λ_{max} (nm)
1a, 2a	$-CH_2CH_2OH$	149–150	81	Orange	411.4
3a, 4a	$-CH_2CH_2OH$	235	42	Orange	433.9
1b, 2b	$-CH_2COOH$	285–586	86	Orange	413
3b, 4b	$-CH_2COOH$	196–197	57	Orange-red	438.4

obtained after cooling was filtered, dried, and recrystallized in ethanol to give yellow crystals. m.p., 85–186°C; yield, 81%. IR (3400 cm^{-1} broad alcholic OH, 2900 cm^{-1} CH aliphatic, 1720, 1760 cm^{-1} anhydride carbonyl).

Typical Synthesis of Products (Table IV): 3,4-(Thioacetic acid)-7H-benzimidazo (a-1,2)benz[dee]iso quindine-7-one

First 0.05 g (0.15 mmol) of 4-(thioacetic acide)naphthalic anhydride and 0.017 g (0.15 mmol) of orthophenylendiamin in 10 ml of glacial acetic acid were refluxed for 2 h. The solution was cooled and filtered, and the crude product was recrystallized in ethanol. m.p., 285°C; yield, 85%.

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