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An Efficient Method for the Synthesis of New Non-Symmetrical Naphthalenediimides

José A. Alatorre-Barajas,[a] Sandy D. Ramírez-Zatarain,[a] Adrián Ochoa-Terán,*[a] Jesus Cordova,*[b] Edgar A. Reynoso-Soto,[a] Daniel Chávez,[a] Valentín Miranda-Soto,[a] Victoria Labastida-Galván,[c] and Mario Ordoñez[c]

Herein we report an efficient synthesis of a series of non-symmetrical naphthalenediimides (NDIs) bearing different neutral, electron-donating and electron-withdrawing groups in the imide moieties. The success of this method is based in the regioselective synthesis and isolation of pure carbamoyl naphthoic anhydride acid intermediates (CNA) in good yields (54 to 99%) and high purity, from the reaction of naphthalene-tetracarboxylic dianhydride acid (NDA) with one equivalent of different primary amines and THF as solvent. The CNA intermediates were refluxed in toluene and gave the naphthalenemonoimides (NMI) in 55 to 89% yields and high purity. The *N*-benzyl NMI was used as starting material in the synthesis of non-symmetrical NDIs (**1 a**-**m**) in 27 to 80% yield with several amines bearing different substituted benzylic groups. In addition, this methodology was extended to obtain other new NDIs (**1 n**-**r**) in good yields (67-90%) and purity.

Introduction

1,4,5,8-naphthalenediimides (NDIs) (Figure 1) are a class of organic molecules that present very useful chemical properties exhibiting a wide variety of applications in the fields of materials science and supramolecular chemistry.[1–7] Based on their electron-withdrawing nature, the NDIs have the ability to experience donor-acceptor interactions,[8–15] thus photovoltaic and semiconductor devices have been constructed.[16–23] In addition, the naphthyl core can be functionalized by attachment of electron-withdrawing substituents to generate electro-optically active molecular materials.[24–28] NDIs have also shown useful biological applications, such as water-soluble NDI derivatives with DNA intercalator properties.[29–34] In addition, a triplet state is efficiently generated when NDIs are subjected to UV irradiation under aerobic conditions, producing singlet oxygen in high yields, making them appropriate compounds for potential photodynamic therapy.[35–37]

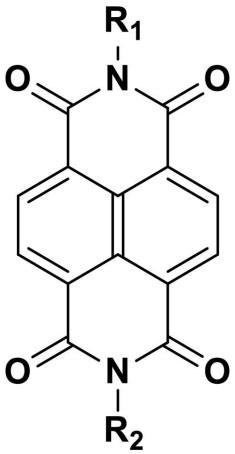

Figure 1. Symmetrical naphthalenediimides $R_1 = R_2$, Non-symmetrical naphthalenediimides $R_1 \neq R_2$.

Despite their useful properties and the wide field of applications and the simplicity of the condensation reaction between the anhydride and amine groups, the preparation of new NDIs in solution synthesis protocols still being limited due to their insolubility in different polar or non-polar solvents and the undesired by-products obtained due to inefficient condensation conditions. Literature search reveals no simple preparation of symmetrical and non-symmetrical NDIs with high yields and purity in a controlled manner under relatively mild conditions.[38]

Symmetrical NDIs with a long alkyl chains attached to the imide increase their solubility in organic solvents and hence facilitate the purification by column chromatography.[39] While, the NDIs bearing aromatic or polar groups usually are purified by re-crystallization method. The yields of the purified products

[a] *J. A. Alatorre-Barajas, Dr. S. D. Ramírez-Zatarain, Dr. A. Ochoa-Terán, Dr. E. A. Reynoso-Soto, Dr. D. Chávez, Dr. V. Miranda-Soto*
Centro de Graduados e Investigación en Química. Tecnológico Nacional de México/Instituto Tecnológico de Tijuana. Bulevar Alberto Limón Padilla S/N, Mesa de Otay, Tijuana, B. C. 22500 México.
E-mail: ochoa@tectijuana.mx

[b] *Dr. J. Cordova*
Chemistry Department, California Lutheran University, 60 West Olsen Rd, Thousand Oaks, California 91360, USA.
E-mail: jcordovaguerrero@callutheran.edu

[c] *V. Labastida-Galván, Dr. M. Ordoñez*
Victoria Labastida-Galván, Dr. Mario Ordoñez
Centro de Investigaciones Químicas-(IICBA), Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Colonia Chamilpa, Cuernavaca, Mor. 62209 México.

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