

Theoretical DFT studies of pyridazine based push-pull π -conjugated heterocyclic systems for SHG nonlinear optics

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INTRODUCTION

Among the numerous classes of π -conjugated organic systems, push-pull substituted heterocyclic compounds are of great interest because it has been experimentally and theoretically demonstrated that they increase the second-order molecular nonlinear optical (NLO) properties response of push-pull chromophores with respect to aryl analogues. In fact, the incorporation of heterocycles into the π -conjugated systems is a powerful approach for tuning the optoelectronic properties because the heterocycles bring higher polarizability, modulate the conjugation pathway, and behave as auxiliary electron donors/acceptors [1]. Therefore a series of push-pull pyridazines were designed in order to understand how structural modifications influence their NLO properties.

RESULTS

Design of the NLOphores. Motivated by previous studies [1], as well as our experience in the design, synthesis and characterization of push-pull heterocyclic π -conjugated systems for a variety of nonlinear optical applications (SHG, TPA) [2] we decided to expand our earlier experimental and theoretical studies to a novel series of five pyridazine-based push-pull heterocyclic systems. The electron-deficient pyridazines **1a-e** (Figure 1) are functionalized with a thiophene electron-rich heterocycle at position 6 and different aromatic and heteroaromatic moieties (phenyl, thienyl, furanyl) functionalized with electron acceptor groups (formyl, cyano and nitro) at position 3.

DFT calculations were carried out to obtain information on conformation, electronic structure, electron distribution, dipolar moment, and molecular nonlinearity response of the push-pull pyridazine derivatives **1a-e**. Calculations were performed at the B3LYP level with the 6-311G** basis set and a polarizable continuum model with dioxane as the solvent. Hyperpolarizability factors were estimated using an incident wavelength of 1064 nm.

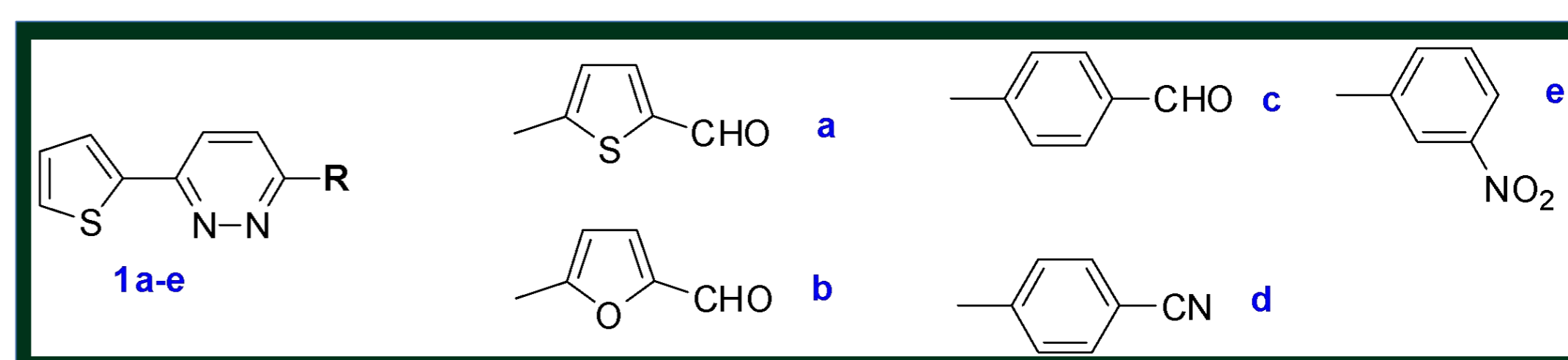
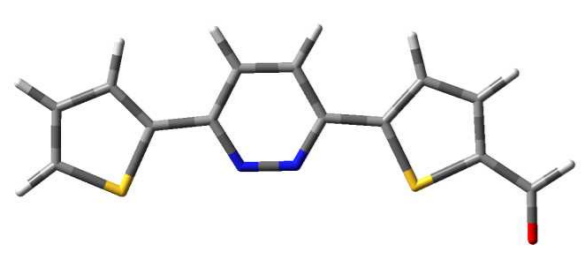
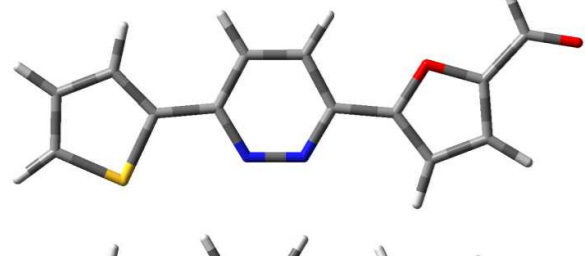
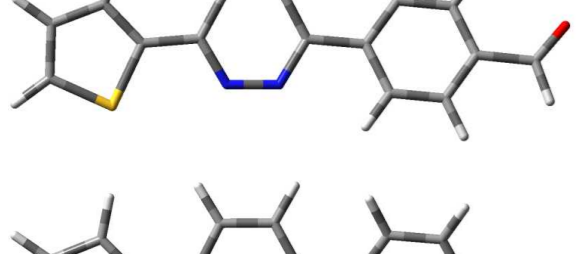
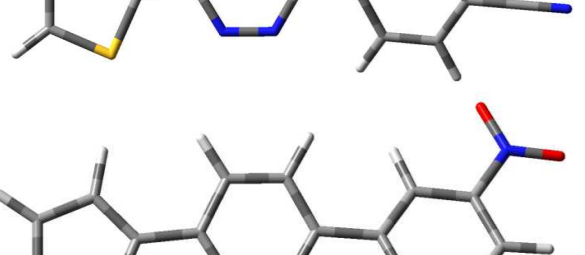



Figure 1. Structures of pyridazine derivatives **1a-e**.

Table 1. Computational result summary of chromophores **1a-e** hyperpolarizability calculations, for the optimized geometry of the lowest energy conformer.

Compound	μ (D)	β_{\parallel} (10^{-30} esu)	β_{tot} (10^{-30} esu)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
	8.98	53	89	-6.27	-2.73	3.54
	5.56	43	71	-6.24	-2.63	3.61
	5.33	56	94	-6.35	-2.56	3.80
	8.04	41	69	-6.40	-2.50	3.90
	4.35	29	48	-6.41	-2.79	3.62

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