

DESIGN OF MOLECULAR MATERIALS FOR NON-LINEAR OPTICS BASED ON
ALKAPLANES AND FENESTRANES DONOR GROUPS

Marcus Vinicius Pereira dos Santos^{1,2}, Ricardo Luiz Longo¹, Rodney J. Bartlett², Ajith Perera²

¹Universidade Federal de Pernambuco-Recife, Brazil

²Quantum Theory Project, University of Florida-Gainesville, Florida 32611, USA

We have investigated the spectroscopic and non-linear optical (NLO) properties of hydrocarbons containing (quasi-)planar tetracoordinated carbon atoms, particularly, fenestranes¹ and alkapanes². These compounds are well known for their low ionization energies (IE). Thus, they can be used as donors in Acceptor-Bridge-Donor (A-B-D) systems. Structures and vibrational frequencies were performed at B3LYP, MP2 and CCSD levels with 6-311+G(2d,p) basis sets. Static polarizabilities (α) and first hyperpolarizabilities (β) were calculated at the PBE1PBE/6-311G(d,p) level. Isotropic shieldings were calculated at the B3LYP/aug-pcS-2 level for the (quasi-)planar carbon atoms and at the B3LYP/6-311G(d,p) level for the other atoms.

Table 1. Influence of the ionization energies of the donor systems due to amine groups

	Donor	B3LYP/6-311+G(d,p)		MP2/6-311+G(2d,p)		CCSD/6-311+G(2d,p)	
		IE (eV)	ν_1 (cm ⁻¹)	IE (eV)	ν_1 (cm ⁻¹)	IE (eV)	ν_1 (cm ⁻¹)
I	[5.5.5.5] fenestrahexene	6.53	122	6.68	122	6.92	122
II	[5.5.5.5]-tetraamine- fenestrahexene	5.33	64	5.63	66	-	-

According to the Table 1, the presence of amine groups decreases more than 1 eV the IE, probably by withdrawing electron density from the central ring. When these systems are connected to diethenylsilane (III)³ and polienic-mesoionic (IV) bridges⁴; and tricyanovinyl (V) and nitrobenzyl (VI) acceptors, we have potential molecular materials for non-linear optics. In Table 2, we present the values of α and β for systems based on donors I and II. The diethenylsilane (III) bridge is more efficient than the polienic-mesoionic (IV) ones. In addition, the smaller IE of Donor II compared to the Donor I leads to larger values for α and β . The isotropic shieldings of the central carbon atom (C1) of fenestranes and its neighboring atoms (C2, C3, C4 and C5) are correlated to the dihedral angle (ω_{donor}) of the (quasi-)planar carbon.

Table 2. Static polarizabilities (α) and first hyperpolarizabilities (β) for some A-B-D systems.

A	B	D	α_{avg} (10 ⁻²⁵ cm ³)	β_{mol} (10 ⁻³⁰ cm ⁵ esu ⁻¹)	Isotropic shielding (ppm)					ω_{donor} (°)
					C1	C2	C3	C4	C5	
V	III	I	5033	48480	65	-3	-8	3	-10	24.5
V	IV	II	2133	3294	79	43	4	27	10	26.4
VI	IV	II	2348	5148	79	44	2	23	15	26.2
VI	III	II	5062	56831	70	30	4	30	6	25.6
V	III	II	16699	120002	70	30	6	31	6	25.6

We conclude these molecular materials based on donor groups and diethenylsilane bridge are potential candidates for non-linear optics applications since they have the largest values of α and β reported^{3,4}. Also, these molecular materials allow fine control of isotropic shielding and other molecular properties by the planarity of the central carbon in the donor group.

1. VENEPALLI, B. R.; AGOSTA, W. C. *Chem. Rev.* 87 (1987) 399-410.
2. RASMUSSEN, D. R.; RADOM, L. *Ang. Chem. Int. Eng. Ed.* 38 (1999) 2875-2878.
3. BRENNAND, R. A.; MACHADO, A. E. D. A. *Engineering* 10 (2010) 219-226.
4. MACHADO, A. E. D. A.; da GAMA, A. A. D. S. *J. Braz. Chem. Soc.* 19 (2008) 1381-1387.