Supplemental Material

Electronic Structure Analysis of the Nonlinear Optical Materials 4-Nitropyridine *N*-oxide (NPO) and 3-Methyl-4-nitropyridine *N*-oxide (POM).

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Abstract. The molecules 4-nitropyridine *N*-oxide (NPO) and 3-methyl-4-nitropyridine *N*-oxide (POM) and the models nitromethane and *N*-methylnitrone were studied with ab initio electronic structure theory at the RHF level and with the inclusion of electron correlation using perturbation and density functional theories. At the highest level, MP2(full)/6-311G**//MP2(full)/6-31G*, the dipole moments μ(NPO) = 0.97 and μ(POM) = 0.89 Debye were obtained. Methyl substitution leads to only a small reduction of μ < 0.1 Debye and the computed dipole moments are in excellent agreement with recent experimental data. The dipole vector of NPO points away from the nitro group (- pole) toward the NO group (+ pole) and the dipole vector in POM is rotated such as to point toward the Me-substituted half. The electric quadrupole moments of NPO and POM indicate quadrupolarity {- + -} along all axes and the $|Q_{zz}|$ values are particularly large. Natural Population analysis reveals the common electronic motif for NPO and POM consisting in an electron-deficient hydrocarbon midsection embedded between electron-rich functional groups. The dipole direction in the pyridine *N*-oxides thus does not reflect contributions by the quinoid resonance form (electron density shifts from the NO to the NO_2 group) to the ground state electronic structure. The directions of the molecular dipole moments of the pyridine *N*-oxides are the simple result of vector addition of the two inward pointing dipoles that are associated with the functional groups and caused by electronegativity differences. In contrast to X-ray electron density studies, the electronic consequences of H/Me replacement are found to be localized. Approximate "molecular dipole moments" based on point charge models (PCM) are compared to the correct dipole moments. The analysis of the PCM derived dipole moments shows that a discussion of solid state effects on the molecular dipole moments of NPO and POM must be postponed until the true dipole moments in the crystal have been more rigorously established.

Table S1, Part A. Total Energies, Number of Imaginary Frequencies, and Vibrational Zero-Point Energies of NPO and POM.

Method	NPO		POM	
	E_{tot}	VZPE[a]	E_{tot}	VZPE[a]
RHF/6-31G*	-524.939150	65.11	-563.974108	83.88
MP2(full)/6-31G*	-526.506592_5		-565.681124	
Becke3LYP/6-31G*	-527.946744	60.13	-567.263095	77.81
RHF/6-311G**	-525.064061		-564.108228	
MP2(full)/6-311G**	-526.893316		-566.110917	
Becke3LYP/6-311G**	-528.085327		-567.411367	

(a) All structures are minima.