Dipole moments of the nonlinear optical materials NPO and POM

Grace Shiahuy Chen, ChangSheng Liu, Rainer Glaser* and John F. Kauffman*

Department of Chemistry, University of Missouri-Columbia, Missouri 65211, USA

Solution-phase measurements and *ab initio* quantum-mechanical calculations (MP2/6-311G//MP2/6-31G*) of the dipole moments of 4-nitropyridine *N*-oxide (μ_{exptl} = 0.83 ± 0.04 D, μ_{calc} = 0.97 D) and 3-methyl-4-nitropyridine *N*-oxide (μ_{exptl} = 0.69 ± 0.05 D, μ_{calc} = 0.89 D) show that the electronic effects of methyl substitution are localized and much smaller ($\Delta\mu$ < 0.2 D) than had previously been thought.**

Zyss *et al.* demonstrated that molecular nonlinear optical properties[1] can be realized with materials with nearly vanishing dipole moments.[2] Substitution in the 4-position of pyridine *N*-oxide (PO) provided an opportunity to accomplish near dipole cancellation and 4-nitropyridine *N*-oxide (NPO) and 3-methyl-4-nitropyridine *N*-oxide (POM) were found to be efficient second-harmonic generation (SHG) materials in solution. NPO crystallizes in centrosymmetric space groups ($P2_1/c$ and $Pnma$), but Sigelle *et al.* showed that POM retains NLO properties in crystals ($P2_12_12_1$).[4] POM has become an important and commercially used organic NLO material.[5]

The structure and the dipole moment of NPO have been well characterized. Katritzky *et al.*[6] and Yamakawa *et al.*[7] reported dipole moments μ(NPO) of 0.69 and 0.88 D, respectively, in benzene solution at 25 °C. The structure of NPO was determined at 30 K *via* X-ray and neutron diffraction.[9] Coppens *et al.* developed a method to assign net atomic charges *via* X-ray refinement[10] (Table 1) and an approximate value of μ(NPO) = 0.4 D was derived from the point charge model. All methods agree that μ(NPO) is small and the solution data indicate 0.8 ± 0.1 D. The structure of POM also has been well characterized. However, no solution dipole moment measurement has been reported due to its low solubility and estimates of μ(POM) are provided only by solid-state and gas-phase studies. An approximate molecular dipole moment of 3.5 D was derived from the point-charge model (Table 1) obtained *via* κ refinement.[11] Semiempirical[12] and *ab initio*[13] calculations suggested dipole moments for POM between 0.22 and 0.48 D. The brief review demonstrates the significant attention that has been dedicated to NPO and POM and stresses the great difficulties in both the measurement and the theoretical prediction of their dipole moments. The present study was undertaken to establish firmly the dipole moment of POM in solution and in the gas phase and we are discussing the parent system NPO as well to ascertain the quality of the methods. We succeeded in the determination of the dipole moment of POM in solution with a new integrated circuit design that allows for the accurate measurements of relative permittivities (ε) at lower concentrations than was previously possible.[14] Predictions of magnitude *and* direction of the dipole moment of NPO and POM in the gas phase are made with *ab initio* calculations that greatly exceed previously achievable levels.

Table 1 Atomic charges derived by natural population analyses and κ refinement of NPO and POM[a]

	NPO[c]		POM[c]	
Atom	MP2	X-Ray	MP2	X-Ray
C^3R[b]	0.04	−0.04	0.06	0.29
Σ(NO)	−0.33	−0.05	−0.34	−0.22
$\Sigma(C_5H_3R)$	0.57	−0.10	0.58	0.52
$\Sigma(NO_2)$	−0.23	0.14	−0.24	−0.32

[a] MP2(full)/6-311G**//MP2(full)/6-31G*. [b] The entry C^3R refers to C^3H and C^3Me, respectively. [c] Atomic charges derived from the populations *P* determined *via* κ refinement taken from refs. 10 (NPO) and 11 (POM).

Evaluation of the Clausius–Mosotti equation relies on the accurate measurement of the ε *via* the frequencies of an LC electrical oscillator setup.[15] The relative accuracy in the determination of ε imposes a lower limit on the solubility of the dipolar solute. With the new device it has now become possible to measure dipole moments at very low concentrations and/or to measure very small dipole moments at millimolar concentrations. The ε(c) of NPO and POM solutions were measured at 25 °C and the refractive indices *n*(c) were measured with an Abbé type refractometer at 532 nm for series of benzene solutions. The slopes, *m*, of the functions $[(\varepsilon-1)/(\varepsilon+2)]-[(n^2-1)/(n^2+2)]$ with respect to solute concentration were used to determine the dipole moments *via* eqn. (1).

$$\mu = 7.0189\,(T/300)^{1/2}m^{1/2}\ \text{(Debye)} \qquad (1)$$

The dipole moments resulting from the slopes of the plots shown in Fig. 1 and eqn. (1) are μ(NPO) = 0.83 ± 0.04 and μ(POM) = 0.69 ± 0.05 D. The present measurement and the previous measurements[6,7]—all carried out under the same conditions—thus indicate μ(NPO) = 0.8 ± 0.1 D. The earliest value might be somewhat low due to aggregation.† Our value and the one reported by Yamakawa *et al.*[7] agree within their respective standard deviations. A possible cause for the deviation between these values might lie with the wavelength used in the measurement of the refractive index.‡ In any case, the excellent result obtained for μ(NPO) gives us great confidence in the accuracy of μ(POM). We conclude that methyl substitution affects the dipole moment only very slightly and leads to a small reduction of 0.14 ± 0.10 D.

NPO and POM were optimized in C_{2v} and C_s symmetry, respectively, at the second-order Møller–Plesset level of

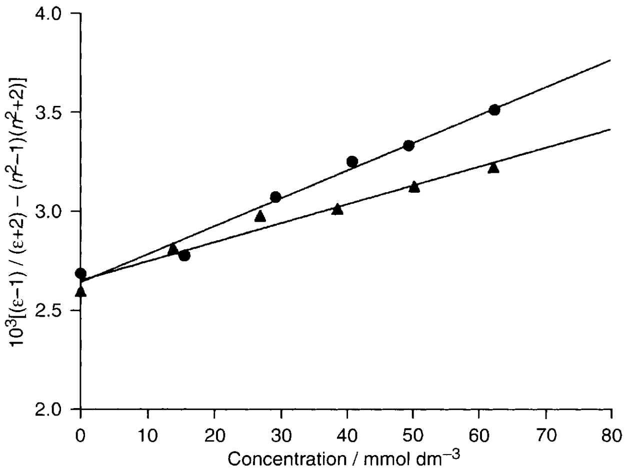

Fig. 1 Plots of the Clausius–Mosotti functions (▲ POM) and (● NPO) *vs.* concentration in benzene solution at 25 °C

perturbation theory with the 6-31G* basis set.[16] We also performed calculations with the more fully polarized valence triple-ζ quality basis set 6-311G**, MP2(full)/6-311G**//MP2(full)/6-31G*, since electrical properties are known to be sensitive to the flexibility of the basis set. The optimized structures of NPO and POM (Fig. 2) are in excellent agreement with experiment. The dipole moment of NPO is directed from the NO_2 group (− pole) toward the NO group (+ pole). Methyl substitution rotates μ(POM) toward the methyl group (Fig. 2). The steric interactions between the nitro and the methyl groups widen the C(3)–C(4)–N(8) and C(4)–C(3)–R(11) angles by 3° and *ca.* 5°, respectively, and cause a rotation of the N–O bond dipole moment components in the direction indicated by μ(POM). As with the solution data, our best estimates of μ(NPO) = 0.97 D and μ(POM) = 0.89 D show a small difference with μ(NPO) being slightly larger than μ(POM) and both values are about 0.2 D higher than the values measured in solution.

The results of the natural population (NP) analysis[17] for NPO and POM are summarized in Table 1. The NP analysis yields atomic charges that are in close agreement with charges derived from topological electron density analysis[18] and the consistency of the latter with all kinds of experimental data has been established.[18] The charges of the functional groups NO and NO_2 and of the hydrocarbon mid-section indicate a quadrupolar electronic structure in which more than 0.5 e was removed from the mid-section. Moreover, they indicate that more negative charge is accumulated on the NO group than on the NO_2 group. The basic electronic motif is common and the variations between NPO and POM are marginal (<0.02) with the only exception concerning C(3) and the attached group (H or Me). While atomic charges are hardly affected by the 3-methyl substitution in the theoretical analysis, significant differences occur between the charges P derived for NPO and POM *via* κ refinement. The P data for POM agree better with the NP data and both methods reflect the quadrupolar motif but the NPO data fail to do so. The NPO P data deviate generally more and they even indicate a positive charge on the NO_2 group which is and electronegativity. While the electron density analysis of NPO by Coppens *et al.*[10] was an early and pioneering contribution to high-resolution X-ray analysis, refinement methods have evolved in the past two decades and it will be of interest to see whether the more sophisticated aspherical atom refinement methods[19] will resolve this discrepancy.

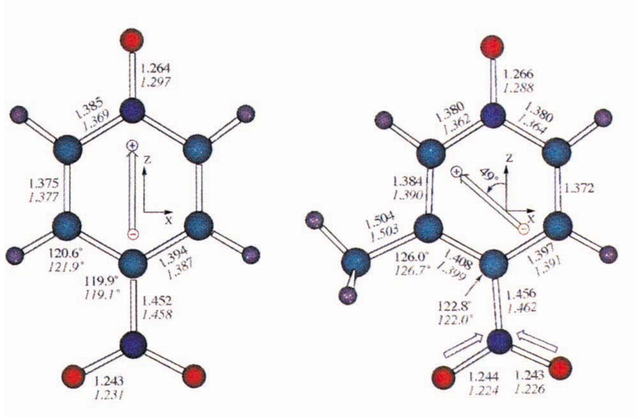

Fig. 2 The MP2/6-31G* optimized structures of NPO and POM agree well with the reported neutron structures (in italics)

Acknowledgment is made to the Research Board of the University of Missouri for support of this collaboration.

Footnotes

[†] Concentrations were not given in ref. 6 and our assumption is based on the state of the measurement techniques at that time. Note also that the authors of ref. 6 estimate the actual error of their measurement to be much larger than the precision error of ±0.02 D and they estimate the actual value of μ(NPO) to be lower (see footnote [†] in their Table 1).

[‡] With $\lambda_{max}(POM) = 346$ nm and $\alpha(\lambda) = \alpha_0/\{1 - (\lambda_{max}/\lambda)^2\}$ (see M. Born and E. Wolf, *Principles of Optics*, 6th edn., Pergamon, New York, 1980, p. 93ff.) one obtains $\alpha(589.3) = 1.53\ \alpha_0$ and $\alpha(532) = 1.73\ \alpha_0$ and a relative change of $\Delta\alpha = 0.2/1.73$ or 11.5% and the dipole moment increases to 0.87D.

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Received, 27th February 1996; Com. 6/01407K