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Molecular and crystal structure of the nonlinear optical material: 2-(*N*-prolinol)-5-nitropyridine (PNP)

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The structure $[C_{10}H_{13}N_3O_3, M_r = 223.23$, monoclinic, $P_{2_1}, a = 5.182(1)$ Å, b = 14.964(4) Å, c = 7.045(1) Å, $\beta = 106.76(1)^\circ$, V = 523.1 Å³, Z = 2, $D_x = 1.42$ Mg mm⁻³, $\mu = 9.0$ cm⁻¹, $F(000) = 236, 23 \pm 1$ °C, $R = (\Sigma ||F_0| - |F_c||/\Sigma|F_0|) = 0.047$ based on 930 reflections with $F_0^2 > 3.0\sigma(F_0^2)$] of this compound reveals it to optimally satisfy many of the structural and symmetry restrictions required for optical second harmonic generation (SHG). The molecules are extraordinarily well aligned to optimize noncritically phase matched SHG with the amino nitrogen to nitro nitrogen charge transfer axis making an angle of 59.6° with the unique axis (b). The mean aromatic plane sits nearly perfectly in the (101) crystallographic plane which may be a natural cleavage surface through which normal propagation may produce noncritically phase matched SHG. Powder optical second harmonic generation measurements ($\lambda = 1.06\mu$; Nd-YAG laser) yield a value of 140.0x relative to powdered urea. Molecules related by a screw operation and the translation [0,0,1] are intermolecularily hydrogen bonded [amino-H/nitro-O; 2.20(10) Å]. The structure is essentially isostructural to the earlier reported structure of N-(4-nitrophenyl)-(L)-prolinol (NPP) which appears to possess slightly enhanced second harmonic efficiency.

INTRODUCTION

There is currently extensive interest in the nonlinear optical properties of organic compounds.^{1,2} Some organics have intrinsic hyperpolarizabilities many times larger than most inorganics that are optically transparent in the visible and near infrared. The origins of the molecular hyperpolarizability are fairly well understood. Calculational procedures³⁻⁵ can often yield a good approximation for the necessary tensor components, β_{iik} and intuitive reasoning alone can yield a molecule possessing large values for the first and second order hyperpolarizability tensors, $\hat{\beta}$ and $\tilde{\gamma}$, respectively. However, there are many symmetry and structural restrictions which govern these hyperpolarizabilities. Particularly, the $\hat{\beta}$ tensor, being a polar third rank tensor, is only nonzero when a center of symmetry is absent.⁶ Other symmetry elements of the various acentric point groups can further cancel or equate the 27 tensor elements so that an otherwise large microscopic molecular component becomes zero under the macroscopic crystal symmetry. For example, under point symmetry 2 in the crystal reference frame, the twofold symmetry operation (Y as unique axis)

| Γ- | 1 | 0 | 0] |
|----|---|---|------|
| | 0 | 1 | 0 |
| L | 0 | 0 | — 1] |

acting on a molecular reference frame changes the sign of all components d_{ijk} whose indices have an odd number of x's and/or z's (e.g., $d_{xyy} \rightarrow -d_{xyy}$ or $d_{xzz} \rightarrow -d_{xzz}$, but $d_{zyz} \rightarrow d_{zyz}$). The result is that only eight (13 if the permutability of the field terms is ignored) tensor elements, $(d_{14}, d_{16}, d_{21}, d_{22}, d_{23}, d_{25}, d_{34}, \text{ and } d_{36})^7$ in the crystal reference frame can be nonzero. The cubic group 432 is zeroed in this way despite being acentric. Adherence of Kleinman⁸ symmetry also eliminates 422 and 622. The cubic groups are generally not easily phase matchable for the purposes of sum and difference frequency generation. The uniaxial and biaxial groups are most useful in this regard, but even some of these are not noncritically phase matchable (NCPM).9,10 The most populous^{11,12} organic group 222 for instance, is not NCPM.¹⁰ Due to molecular anisotropy, a further mitigating factor involves an orientational dependence of the molecule upon $\tilde{\mathbf{d}}$, the macroscopic hyperpolarizability tensor.¹³ Thus, there are optimal orientations of the microscopic molecular tensor $(\hat{\beta})$ with respect to the macroscopic optical coordinate system. A molecule with a very large molecular hyperpolarizability could suffer from being poorly oriented in the crystalline state with the extreme worse case being a centric crystal. The molecule N,N-dimethyl-4-nitroaniline is a good example of this. Despite a large molecular hyperpolarizability,¹⁴ the crystal structure¹⁵ is only slightly acentric resulting in a very low crystalline hyperpolarizability.^{16,17}

Obviously, solid state structural features represent a significant factor for nonlinear optical behavior. Optimizing a molecule and structure to yield the maximum second harmonic generation (SHG) involves many factors. However, the least controllable factors include in which point group and with what orientation a molecule crystallizes. It is fairly well recognized that the best structural moiety for SHG in the visible regime of 400–500 is p-nitroaniline.^{1,2} The parent molecule is centric in the solid state, so systematic chemical modification has been undertaken to induce derivatives to crystallize acentrically. Reported here is the preparation and molecular and crystal structure of a pyridine analog of pnitroaniline which has been modified such that it crystallizes within a few percent of optimum for its point group. As a result, this material, like its benzene ring analog NPP¹⁹ possesses SHG efficiency¹⁸ comparable or better than any other currently available given the restriction of equivalent transparency.

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EXPERIMENTAL

2-(N-prolinol)-5-nitropyridine (PNP): In a 1 / round bottom flask fitted with magnetic stirbar, addition funnel, nitrogen bubbler, and external water bath was placed 2chloro-5-nitropyridine (47.5 g, 300 mmol, freshly recrystallized from 9:1 isooctane/toluene) and dry N-methylpyrrolidinone (125 ml). To this stirred slurry was added a mixture of L-prolinol (34.4 g, 330 mmol), triethylamine (36.4 g, 360 mmol) and more N-methylpyrrolidinone (25 ml) dropwise over one hour. The reaction was then stirred overnight at room temperature after which time TLC analysis showed the chloropyridine to be completely consumed. The reaction mixture was made slightly acidic with cold 5% aqueous HCl and transferred to a separatory funnel with water (300 ml) and ethyl acetate (300 ml). The resulting phases were separated and the organic phase washed with water (200 ml, $3\times$) and brine (100 ml). The aqueous phase was back extracted with more ethyl acetate (300 ml) which was then washed in an identical fashion. The combined organic phases were dried (MgSO₄), vacuum filtered through sintered glass, and concentrated to a viscous oil by rotary evaporation. The residual oil was redissolved in ethyl acetate (300 ml), silica gel (140 g) was added and then the slurry was concentrated to dryness. The adsorbed crude product was placed at the top of a 1.5 kg column of 40-140 mesh silica gel and eluted with a gradient of ethyl acetate in hexane $(0 \rightarrow 50\%)$. The center fractions were combined to give 50.5 g and the leading and tailing fractions were combined to give 11.8 g more for an overall total of 62.3 g (90.1%). The center cut material was further purified by three subsequent recrystallizations from 4:1 diisopropylether/ethanol to give 25.3 g of highly purified product, m.p. 83°: IR (KBr) 3500, 2940, 2880, 1595, 1430, 1335, 1285, 1175, 1110, 1040, 820, 760 cm⁻¹; NMR (CDCl₃) δ 1.65–2.33 (*m*, 4H), 3.10–3.90 (m, 4H), 4.10-5.00 (m, 2H), 6.35 (d, J = 9, 1H), 8.10 (dd, J)J = 3.9, 1H, 8.86 (d, J = 3, 1H); mass spectrum, m/e (%) intensity) 224 (1), 223 (9, M⁺), 193(13), 192(100), 146 (55).

A sample of NPP was prepared in an analogous fashion by substituting 4-fluoronitrobenzene for 2-chloro-5-nitropyridine.¹⁹

Sample utilized for structure determination was crystallized from isooctane and toluene; yellow prismatic crystal $(0.20 \times 0.20 \times 0.30 \text{ mm})$; mounted with long axis ~ parallel to ϕ axis of goniometer. Enraf-Nonium CAD4 computer controlled kappa axis diffractometer; $\omega - \theta$ scan technique,²⁰ variable scan rate 3° to 20° (ω); data collected to 150°(2 θ), $CuK\alpha(\lambda = 1.541 \ 84 \ \text{\AA})$, graphite crystal incident beam monochromator. Cell constants from 25 reflections $(6^{\circ} < \theta < 41^{\circ})$. Systematic absences $0k \ 0 \ k = 2n + 1$, least squares refinement produce monoclinic spacegroup $P2_1$. Three reflections, measured every 41 min, did not change. 1180 reflections collected, 1125 unique, not systematically absent. No decay or absorption corrections. Lorentz and polarization corrections applied. Linear absorption coefficient: 9.0 cm⁻¹. Secondary extinction correction²¹ applied with least-squares coefficient of 7.6×10^{-6} (abs. units). Solved by direct methods; refined in full matrix least squares; 200 reflections (minimum E 1.30), 2461 relationships produced

64 phase sets. 14 atoms located from E-map, remaining atoms located in succeeding difference Fourier syntheses. Hydrogens atoms located, refined isotropically. Final refinement: 930 reflections with $I > 3\sigma(I)$, 197 parameters, with largest shift 0.17 σ . Highest peak in final difference map: $e/Å^3$. $R = \sqrt{(\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2)} = 0.062;$ 0.19 $w = 4F_0^2/\sigma^2(F_0^2); \ \sigma^2(F_0^2) = [S^2(C + R^2B) + (pF_0)^2]/$ Lp^2 , where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = background count, Lp = Lorentz-polarization factor, p = 0.050 introduced to downweight intense reflections. Scattering factors from Cromer and Waber²²; $\Delta f'$ and $\Delta f''$ are those of Cromer²³; anomalous dispersion effects included in F_c .²⁴ All calculations performed on PDP-11/60 based TEXRAY (trademark Molecular Structure Corporation, 1982) computer using the Enraf-Nonius Structure Determination Package and proprietary programs of Molecular Structure Corporation.

Powder SHG measurements performed with Quanta Ray DCR-1 Q-switched pulsed Nd-YAG laser operating at ~250 mJ/pulse at 1.06 μ . Sample powdered with mortar and pestle, compressed to 1 mm between two 0.05×12.7 mm quartz discs. Incident laser light normal to sample, scattered light collected at 45° on PIN Si diode after passing through two 3 mm BG-38 glass filters and one 532 nm interference filter. Second harmonic signal box car averaged. Identical runs with powdered urea before and after establish signal relative to urea. Measurements of this type on PNP established it as 140x(urea).

Preparation

Preparation of PNP is trivially achieved by reaction of (L)-prolinol and 2-chloro-5-nitropyridine in a dipolar aprotic solvent in the presence of a tertiary amine base:



The requirement for strong donor and acceptor moieties in the same molecule to enhance field dependent polarization also renders the chemist's task more straightforward. Appropriately disposed electron withdrawing groups, particularly nitro groups facilitate aromatic nucleophillic substitution and are also the moiety of choice to maximize molecular hyperpolarizabilities. The optically active amine *l*-prolinol ensures an acentric point group for the product. A large family of materials made in this way has been investigated by systematic reaction of polar halonitroaromatics with a variety of nucleophiles, many of them optically active.^{18,25}

Molecular structural considerations

The final atomic coordinates are given in Table I.²⁶ Bond distances and angles referred to in Fig. 1 are included in Table II, or Table III. Because of the structural similarity to NPP, our discussion of PNP will include some interesting points of comparison with data from NPP coming from that

TABLE I. Atomic coordinates [excluding all hydrogens but H(1)], and isotropic thermal parameters (for nonhydrogens $B_{eqv} = \frac{4}{3} \sum \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$).

| Atom | x | у | Z | B _{eqv} |
|------------|-------------|-------------|-------------|------------------|
| 01 | - 0.5537(6) | - 0.4888(0) | - 0.1928(4) | 4.53(6) |
| O 2 | 0.1488(6) | 0.0169(2) | - 0.5326(4) | 4.68(6) |
| O3 | 0.1855(6) | - 0.1079(2) | - 0.6712(4) | 5.68(7) |
| N1 | - 0.3853(6) | - 0.2494(2) | - 0.0809(4) | 3.05(5) |
| N2 | - 0.1493(6) | - 0.2469(2) | - 0.3108(4) | 3.43(6) |
| N3 | 0.1098(6) | -0.0638(2) | - 0.5507(4) | 3.72(6) |
| C1 | - 0.5730(8) | - 0.3953(3) | - 0.2229(5) | 3.54(7) |
| C2 | - 0.3618(7) | - 0.3467(2) | - 0.0603(5) | 3.23(7) |
| C3 | - 0.3921(9) | - 0.3618(3) | 0.1464(5) | 4.22(9) |
| C4 | - 0.5817(9) | -0.2883(3) | 0.1686(6) | 4.06(8) |
| C5 | - 0.5015(7) | - 0.2078(3) | 0.0660(5) | 3.38(7) |
| C6 | - 0.2689(7) | - 0.2007(2) | - 0.1935(5) | 2.94(7) |
| C7 | - 0.2640(8) | -0.1062(3) | - 0.1858(5) | 3.49(7) |
| C8 | - 0.1418(8) | -0.0606(2) | -0.3038(5) | 3.47(7) |
| C9 | - 0.0226(7) | -0.1093(2) | - 0.4253(5) | 3.18(7) |
| C10 | -0.0300(7) | -0.2006(3) | - 0.4234(5) | 3.54(7) |
| H1 | - 0.442(19) | - 0.514(6) | - 0.225(9) | 13.1(25) |

reported in Ref. 19.27 In both compounds, the aromatic ring is essentially planar with the largest deviation from the least squares plane being 0.009 Å (PNP) and 0.008 Å (NPP). The PNP nitrogens N(1) and N(3) are -0.002 Å and 0.004 Å out of the aromatic least-squares plane, respectively. The corresponding distances in NPP are 0.04 Å and 0.01 Å. The plane of the nitro group is twisted 8.9° out of coplanarity with the pyridine ring, as compared to 5.8° in NPP. In PNP, the nitro oxygens are on opposite sides of the aromatic plane but they are on the same side in NPP. Comparison of nitrogen oxygen bond lengths in both compounds indicates the nitro group in NPP has N-O bonds [1.240(4), 1.236(4) Å] that are slightly longer and may be of a lower bond order than in PNP. In both compounds, the nitro is essentially planar with the attached carbon. In PNP N(3) sits 0.009 Å out of the plane defined by C(9), O(2), and O(3) with the corresponding distance in NPP being less than 0.001 Å.



FIG. 1. ORTEP II of a single molecule of PNP.

TABLE II. Relevant bond distances and angles. See also Table III.

| Atom1 | Atom2 | Distance | Atom1 | Atom2 | Distance |
|-------|------------|----------|-------|-------|----------|
| O2 | N3 | 1.225(4) | N2 | C6 | 1.356(4) |
| N2 | C10 | 1.332(4) | N3 | C9 | 1.437(4) |
| 01 | H 1 | 0.78(10) | C6 | C7 | 1.416(4) |
| C7 | C8 | 1.364(5) | C8 | C9 | 1.396(4) |
| C9 | C10 | 1.367(5) | O3 | N3 | 1.226(4) |
| Atom1 | | Atom2 | Atom3 | | Angle |
| C6 | | N2 | C10 | | 118.1(3) |
| O2 | | N3 | O3 | | 121.8(3) |
| 02 | | N3 | C9 | | 119.8(3) |
| O3 | | N3 | C9 | | 118.4(3) |
| N1 | | C6 | N2 | | 116.5(3) |
| N1 | | C6 | C7 | | 121.7(3) |
| N2 | | C6 | C7 | | 121.7(3) |
| C6 | | C7 | C8 | | 118.8(3) |
| C7 | | C8 | C9 | | 118.6(3) |
| N3 | | C9 | C8 | | 120.2(3) |
| N3 | | C9 | C10 | | 119.9(3) |
| C8 | | C9 | C10 | | 119.8(3) |
| N2 | | C10 | C9 | | 123.0(3) |

While extremely planar the nitro group of NPP appears to be bent slightly out of the aromatic ring at the attached carbon because both oxygens appear on the same side of the aromatic ring. The nitro in PNP is slightly more twisted but otherwise well aligned along the C(6)-C(9) axis. The hydroxymethylpyrrolidine of the PNP molecule is structured closely to that of NPP. Table III should be consulted for comparison of bond lengths, angles, and torsional angles. The nitro-

TABLE III. Comparison of prolinol substituent of PNP and NPP.

| Bond distance | zs | | | | | |
|---------------|---------------|-------|-------|--------|---------------|------------|
| Atoml | A | tom2 | | PN | Р | NPP |
| N1 | | C6 | | 1.342(| 4) Å | 1.361(3) Å |
| N1 | | C5 | | 1.477(| 4) | 1.467(3) |
| C4 | | C5 | | 1.522(| 5) | 1.525(4) |
| C3 | | C4 | | 1.513(| 6) | 1.518(4) |
| C2 | | C3 | | 1.526(| 4) | 1.534(3) |
| N1 | | C2 | | 1.464(| 4) | 1.476(3) |
| C1 | | C2 | | 1.522(| 5) | 1.522(3) |
| 01 | | Cl | | 1.415(| 4) | 1.413(4) |
| Bond angles | | | | | | |
| Atom1 | Atom2 | 1 | Atom3 | | PNP | NPP |
| N1 | C5 | | C4 | | 102.8(3)° | 103.8(2)° |
| C3 | C4 | | C5 | | 104.6(3) | 103.5(2) |
| C2 | C3 | | C4 | | 103.8(3) | 103.9(2) |
| N1 | C2 | | C3 | | 102.3(3) | 102.2(2) |
| C2 | N1 | | C5 | | 112.9(3) | 112.3(2) |
| N1 | C2 | | Cl | | 112.3(3) | 112.1(2) |
| C1 | C2 | | C3 | | 113.5(3) | 112.3(2) |
| 01 | C1 | | C2 | | 110.8(3) | 111.6(2) |
| Torsional ang | les | | | | | |
| Atom1 | Atom2 | Atom3 | A | Atom4 | PNP | NPP |
| C3 | C4 | C5 | | NI | 26.7 | 7° |
| C2 | C3 | C4 | | C5 | - 37.2 | 2 - 38.1 |
| N1 | C2 | C3 | | C4 | 32.3 | 3 32.2 |
| C5 | N 1 | C2 | | C3 | - 16.2 | 2 - 14.7 |
| C2 | N 1 | C5 | | C4 | - 6 .3 | 3 - 8.5 |
| | | | | | | |

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FIG. 2. ORTEP II stereoview of packing of four molecules of PNP and unit cell. Note the proximity of the prolinol hydroxy hydrogen to the nitro oxygens of the molecule related by [0,0,1] translation and screw operation. In this ORTEP the hydrogen-bonded hydrogen [H(1)] has been assigned a thermal spheroid smaller than the actual 13.1 Å² for the sake of clarity.

gen N(1) of PNP sits 0.088 Å out of the plane defined by C(2), C(5), and C(6) and thus is slightly pyramidal, while NPP is slightly more so with a corresponding distance of 0.10 Å. The C(2) and C(5) deviate only -0.187 Å and -0.110 Å, respectively, from the least-squares plane of the pyridine ring. The unpaired electrons on N(1) [defined along a mirror plane that would exchange C(2) and C(5)] are thus only 2.1° (4.7° in NPP) out of conjugation with the pyridine ring. The high degree of orbital overlap will permit a large induced polarization from amine to nitro. The molecular absolute configuration refined for PNP is S, which is verified from the absolute configuration of the precursor *l*prolinol, S(+). This is further verified by an S configuration found for NPP¹⁹ which was also reported to be made from *l*-prolinol. Overall, the PNP and NPP molecules differ relatively little, though there appear to be some slight differences in the nitro and amine groups.

Crystal structural considerations

In both molecules, the weak intermolecular hydrogen bond (Fig. 2) perhaps helps offset the dipolar forces which might otherwise result in a centric structure, and may stabilize electron polarizations toward the nitro group. The O(3)-H(1) intermolecular distance is 2.20(10) Å with an O(3)-O(1) distance of 2.965(4) Å. The corresponding oxygen-oxygen distance in NPP is 2.86 Å suggesting a shorter hydrogen bond and a contraction along the **b** axis. In fact such a contraction in **b** has occurred with the change from 14.964 Å (PNP) to 14.908 Å (NPP). The expansion of the **b** axis in PNP has been accompanied by slight contractions

TABLE IV. Comparison of prolinol substituent of PNP and NPP. Deviation from aromatic least-squares plane.

| Atom | PNP | NPP |
|------|---------|---------|
| N1 | 0.002 | 0.036 |
| C1 | - 1.122 | - 0.942 |
| C2 | 0.187 | 0.320 |
| C3 | 0.828 | 0.957 |
| C4 | 0.221 | 0.267 |
| C5 | 0.110 | 0.120 |
| 01 | - 0.919 | - 0.666 |

along a and c such that the cell volume (523.1 Å) has overall decreased relative to NPP (543.8 Å³).¹⁹ For PNP, the distance between (101) planes is 3.540 Å which is 0.125 Å less than in NPP. The reason for the cell reduction in PNP in the ac plane is not readily apparent. One might expect the atoms of the PNP prolinol to deviate less from the aromatic plane. However, while this is true for most of the atoms the most wayward atom of PNP's prolinol [C(1)] is almost 0.2 Å further from the aromatic plane than for the corresponding atom of NPP (see Table IV). Most likely, the unit cell differences along a and c are a further result of subtle differences in the hydrogen bonding geometry. All else being equal, the slight decrease in cell volume for PNP should result in a proportional increase in volume hyperpolarizability (+4%). Of course, this may be offset by an expected decrease in molecular hyperpolarizability of PNP relative to NPP (vide infra).

The molecular least-squares plane (through the six aromatic carbons) of NPP was found to intersect the **ac** plane essentially perpendicularily and making an angle of less than 0.1° (not the 11° reported in Ref. 19) with the (101) crystallographic plane. An analogous situation exists in PNP with the angle being 0.5°. As suggested for NPP¹⁹ the (101) is a likely cleavage plane for PNP.

For point group 2 and approximating the molecule as one dimensional, in terms of induced polarization, Zyss and



FIG. 3. ORTEP II view of PNP unit cell down b axis. Also shown are the various axes described in the text. Note the molecular (aromatic ring) plane parallel to the crystallographic (101) plane.

Oudar¹³ have shown that there are two major macroscopic tensor components, YYY and YXX²⁸ (the coordinate system is defined by the intersection of the molecular plane with the **ac** plane; this intersection is the X axis; see Fig. 3). The relationship between these macroscopic components and the microscopic polarization are

$$d_{YYY} \propto \cos^3 \Theta,$$

 $d_{YXX} \propto \cos \Theta \sin^2 \Theta,$

where Θ is the angle between the molecular polarization axis and the Y optic axis (under point symmetry 2 this is the unique crystallographic axis b). The optimum angle for d_{YYY} is 0° and for d_{YXX} is 54.74°. The latter tensor component achieves a lower (38%) conversion, from microscopic to macroscopic polarization, but it can be noncritically phase matchable (NCPM) and d_{YYY} cannot. Thus, the desirable component to optimize towards is YXX. For PNP $\Theta = 59.6^{\circ}$ [one dimensional polarization defined along the N(1) to N(3) vector] so YYY achieves only 13% of its 100% maximum, but the important YXX achieves nearly the full 38% maximum that is possible for this component. This molecule is almost perfectly aligned to maximize the NCPM component. The corresponding angle Θ in NPP is 58.6° and thus is slightly better aligned. However the nitrogen in the pyridine ring will introduce some asymmetry in the ground and excited state electronic structure of PNP. Thus the correct largest polarization may not be precisely along N(1) to N(3), meaning that the slight difference in Θ between the two materials cannot be discussed with significance. The dipole moment of nitroaniline is 6.275 D; pyridine 2.228 D; and 2-amino-5-nitropyridine 5.51 D.²⁹ Vector addition of the experimental pyridine and nitroaniline dipole moments readily gives the experimental dipole moment of 2amino-5-nitropyridine. With some confidence, we can then calculate that the ground state dipole is canted 20.5° off of the amino/nitro axis. This would raise the angle Θ for PNP to 80.1°, for at least the ground state contribution (μ_0) to the polarization change $(\mu_{ex} - \mu_0)$. How two dimensional this



FIG. 4. Electronic spectra in ethanol of NPP and PNP. Concentration of both compounds approx. 5×10^{-5} M.

renders the molecule depends on the magnitude and direction of μ_{ex} . Oudar and Zyss¹³ have determined criteria to experimentally distinguish between the one and two dimensional approximations and found MAP [N-(2,4-dinitrophenyl)methyl alanate] to be clearly two dimensional. Analogous work on PNP and NPP would be of interest to more clearly define the limits of the one-dimensional approximation on *p*-nitroaminoaromatics.

Optical considerations

Since only the one angle Θ need be specified to calculate YYY and YXX, the orientation of X and Z (1X) with respect to either **a** or **c** need not be specified or determined explicitly. In fact, in order for there to be a YXX component without mixing into a YZZ component, the X axis was chosen to coincide with the molecular plane and **ac** crystallographic plane. Under the approximation of a one dimensional polarization the YZZ component then becomes zero. Since X and Z of this coordinate system are not necessarily the orthogonal dielectric coordinate axes, the YXX component may be divided among three other components in the macroscopic crystal:

$$d_{\rm YXX} = \sin^2 \psi d_{\rm yzz} + \cos^2 \psi d_{\rm yxx} + \sin 2\psi d_{\rm yxz},$$

where x,y(\equiv Y \equiv b), and z are the dielectric axes and ψ is the angle of rotation (about Y) between X and x. For the monoclinic lattice x and z are not restricted by symmetry so $x(\perp z)$ may lie anywhere in the ac plane.³⁰ The location of the optic axes must be determined experimentally. This has not been done for either PNP or NPP, but based on straightforward arguments¹⁹ it might be assumed that X and x are nearly coincident. This has been experimentally verified in the case of MAP [N-(2,4-dinitrophenyl)methylalinate] where the two axis systems differ by no more than $1^{\circ,31}$ The d_{yxx} will then contain all of d_{YXX} . Zyss, Nicoud, and Coquillay have discussed the phase matching possibilities for NPP, and suggest two circumstances under which NCPM could occur. It may well be that the large powder SHG efficiencies observed suggest NCPM is occurring. If the optic axes are fixed as suggested above, a propagating direction for NCPM can be predicted. The propagation vector will be fixed in the $XZ(\equiv xz \equiv ac)$ plane, XZ (xz) polarized, and normal to the crystallographic (101) plane. The powder SHG is so large. that the actual room temperature NCPM conditions might be close to this restriction. If the assumptions are correct, then not only is the molecule almost perfectly aligned to project the maximum microscopic hyperpolarizability into macroscopic components, but NCPM SHG occurs with propagation incident on a natural crystal cleavage plane.

Molecular electronic considerations

Figure 4 displays electronic absorption spectra of PNP and NPP in ethanol. As is readily apparent, PNP is blue shifted $(21 \text{ nm} \equiv 0.18 \text{ eV})$ in its lowest energy transition relative to NPP. The solid state electronic spectra of either crystalline material are not available, but the relative differences in the polar hydrogen bonding solid state environment should be comparable. A simple calculation based on the two level system of ground and first excited state has been proposed³² to rationalize the difference in molecular hyperpolarizabilities between closely related molecules. The charge transfer (ground to first excited state) hyperpolarizability β_{ct} is given by

$$\beta_{\rm ct} = \frac{3e^2\hbar^2}{2m} \mathcal{F}(W) f\Delta\mu_{\rm ex},$$

where f is the oscillator strength, $\Delta \mu_{ex}$ is the difference between ground state (μ_0) and first excited state (μ_{ex}) dipole moments, and

$$\mathcal{F}(W) = \frac{W}{[W^2 - (2\hbar\omega)^2][W^2 - \hbar\omega)^2]}$$

Here W is the transition energy for the first excited state and ω is the laser fundamental frequency. For PNP and NPP if the difference in oscillator strengths and $\Delta \mu_{ex}$ are small, then all else being equal, the weighting by $\mathcal{F}(W)$ governs the difference in β between different compounds. For PNP W = 3.35 eV, and for NPP W = 3.17 eV. Thus, for $\hbar\omega = 1.165 \text{ eV} (\lambda = 1.06 \ \mu), \ \mathcal{F} (3.35 \ \text{eV})/\mathcal{F} (3.17)$ eV) = 0.742. The molecular hyperpolarizability of PNP should be \sim 75% that of NPP. Normalizing by the difference in volume hyperpolarizability should increase this slightly. This is a fairly crude estimate; a more accurate comparison can be had by semiempirically calculating the transition energies and components between "all" states, and then summing over all contributions to the molecular hyperpolarization.^{3-5,33} What is lost in hyperpolarizability may be made up in transparency. A 0.18 eV shift in the absorption edge should make PNP at least somewhat more transparent $(NPP \sim 90\%)^{19}$ to the Nd-YAG second harmonic.

CONCLUSIONS

For some time, chemists have been trying to prepare the best material possible for second harmonic generation (as well as other nonlinear applications). Organics were finally set on because of their large molecular hyperpolarizabilities, and the p-nitroaniline (pNA) moiety was found to be premier in this regard, given its transparency. Because of the symmetry and orientational restrictions a large number of pNA derivatives were synthesized by many investigators in the hope of achieving the optimum of all of the controlling factors. Because of the near perfect projection from the microscopic to macroscopic hyperpolarizability, and the coincidence of the molecular plane with the (101) plane which perhaps facilitates easy NCPM, both PNP and NPP can be considered maximally optimized for their class of molecule.³⁴ It may prove a great challenge to prepare another crystalline nitroaniline or aminonitropyridine compound which will significantly improve on them.³⁵ The question of long term stability in the laser has not been investigated, but if both of these materials are damage resistant, further synthesis of pNA compounds (for the purposes of SHG) may not be justified. Both PNP and NPP need be investigated as single crystals to verify the propositions presented here. The pyrazine and two possible pyrimidine derivatives, and remaining pyridine derivative should be prepared for sake of further comparison. The isostructurality of PNP and NPP provide an ideal opportunity to compare organic materials which essentially only differ at a specific atomic site. If these

other derivatives are also isostructural, then a series of six materials will be available to investigate the subtleties of atomic replacement without having to contend with other major structural changes.

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- ²⁷In the course of recalculating various structural parameters for NPP from data in Ref. 19, we have found that three of the reported atomic coordinates must be in error involving changes in sign. These are (using numbering scheme of Ref. 19): C1 (correct y component is -0.0095), C2 (correct y component is +0.0840), and H14 (correct y component is -0.403).
- ²⁸The x, y, and z orthogonal molecular axes (not to be confused with the non*italicized* dielectric axes x,y,z) are defined such that the xy plane is in the aromatic molecular plane [y coincident with the N(1) to N(3) vec-

tor] and z is perpendicular to it. The polarization or susceptibility to polarization is assumed negligible in the z direction. Since the molecular plane is perpendicular to the XZ (\equiv ac) plane, z coincides with Z, meaning all Z subindexed components must be zero. This is different from the general situation presented in Refs. 13 and 29 (where the surviving components are the YYY and YZZ following the one-dimensional restriction) but can be easily verified by working through Eqs. (4a)-(4d) of Ref. 31.

- ²⁹Dipole moments determined in benzene as solvent (at 25 °C); average of values from: A. L. McClellan, *Tables of Experimental Dipole Moments* (Freeman, New York, 1963); A. L. McClellan, *Tables of Experimental Dipole Moments* (Rahara, El Cerrito, Calif., 1974), Vol. 2.
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- ³⁴It could be argued that since the pyridine nitrogen introduces significant asymmetry in the ground state dipole moment μ_0 , the alignment is really

not as nearly ideal. However the real quantity of interest is $(\mu_{ex} - \mu_0) = \Delta \mu_{ex}$. Breaking the PNP first excited state dipole moment into its pyridine and *p*-nitroaniline "components," the first excited state dipole moment of the *p*-nitroaniline component is probably much larger than for the pyridine component, dominating μ_{ex} , so that the quantity $\Delta \mu_{ex}$ is brought back more closely toward ideal.

³⁵This may not quite be true of the case for electro-optics where phase matching is not a concern. Under those circumstances one wants to optimize whatever component gives the maximum conversion from microscopic to macroscopic hyperpolarizability. This will be the YYY which can convert 100% (2.6 times better than YXX). The compound MNA [2-methyl-4-nitroaniline; G. F. Lipscomb, A. F. Garito, and R. S. Narang, J. Chem. Phys. 75, 1509 (1981); see also Ref. 13] is within ~20° of perfect alignment, and as a consequence has been found to display a large electro-optic effect. Simple calculation (Ref. 13) can show that 20° is within 17% of perfect alignment. Thus some improvement can still be had.