New nonlinear-optical organic crystal: 4-dimethyl-aminobenzaldehyde-4-nitrophenyl-hydrazone

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Single crystals of 4-dimethylaminobenzaldehyde-4-nitrophenylhydrazone were grown from solution. We determined their linear-optical (absorption and refractive indices) as well as their nonlinear-optical properties. From the highest nonlinear-optical coefficient \( d_{12} = 270 \text{ pm/V} \) at \( \lambda = 1.542 \mu \text{m} \) we determine an effective nonlinear-optical coefficient \( d_{33}^\text{eff} \approx 150 \text{ pm/V} \) for phase-matched frequency doubling that is, to the best of our knowledge, the largest reported phase-matchable coefficient. The nonlinear-optical properties are discussed in terms of the crystal structure and the molecular hyperpolarizabilities. In addition, the phase-matching configurations for second-harmonic generation and optic parametric oscillation are derived.

1. INTRODUCTION

Following the development of reliable, compact, and powerful semiconductor laser diodes, new materials with large nonlinear-optical properties in the near infrared have engendered great interest. Whereas inorganic materials are most efficient at shorter wavelength, organic compounds are promising candidates for electro-optical materials.1,2 They are distinguished from other organic materials by their increased nonlinearities and their high tendency to form noncentrosymmetric crystal packing. Some hydrazone derivatives were previously investigated in nonlinear optics for the preparation of crystals and Langmuir–Blodgett films, were characterized by the powder test of Kurtz and Perry, or were investigated in more detail.1,3–10

We have grown single crystals of one of these new compounds, 4-dimethylaminobenzaldehyde-4-nitrophenylhydrazone (DANPH) (Fig. 1). The molecule consists of a main chain composed of two phenyl rings tilted at an angle of 11.8° that are connected through the hydrazone backbone (–C=N—N—). We define the charge-transfer axis by the nitrogen atoms (N1) and (N4) of the donor group (H3C)2N and the acceptor group (NO2), respectively. The highly polarizable \( \pi \) electrons give rise to large first-order hyperpolarizabilities of the molecule. This fact was quantitatively established with electric-field-induced second-harmonic-generation measurements, which led to values of \( 200 \times 10^{-36} \text{ m}^4 \text{ V} \) at \( \lambda = 1.907 \mu \text{m} \) for the first-order hyperpolarizability \( \beta_{zzz} \) and of \( 153 \times 10^{-36} \text{ m}^4 \text{ V} \) for the molecular hyperpolarizability extrapolated to infinite wavelengths.2 Here we report on the linear- and nonlinear-optical properties of single crystals of DANPH and show that the second-order nonlinearities are comparable with those of the best available organic crystal for nonlinear optics, 4-\( N,N \)-dimethylamino-4′-\( N′ \)-methylstilbazolium toluene-\( p \)-sulfonate (DAST).11–15

2. CRYSTAL GROWTH AND STRUCTURAL PROPERTIES

DANPH crystallizes in three different structures [structure I (\( P2_12_12 \)), structure II (Cc), and structure III (\( P2_1/c \))]. The growth of these different structures depends strongly on the crystallization conditions. The first structure consists of a cocrystallization of DANPH (first synthesis of DANPH) with benzene at a ratio of 4 to 1 (structure I, space group \( P2_12_12 \)).4 Unfortunately, the unfavorable orientation of the molecules in the crystal lattice is detrimental for large second-order nonlinear-effects. Crystals of the second structure (structure II, space group Cc) are obtained from a fast crystallization in acetonitrile and grow as red-greenish prisms that are highly efficient in the second-harmonic powder test at \( \lambda = 1.3 \mu \text{m} \) (signals of the same order of magnitude as for DAST). The third structure is obtained by slow crystallization in ethanol and appears macroscopically as centrosymmetric, well-formed, red-orange plates (structure III, space group \( P2_1/c \)).2 More details of the crystal growth can be found in Ref. 16.

Here we report experimental results for the most interesting noncentrosymmetric crystal structure II. Hereafter we drop the designations I, II, and III and refer to crystals of structure II as DANPH. Crystallographic data can be found in Table 5 of Ref. 2. DANPH crystallizes in the noncentrosymmetric space group Cc (point group \( m \)), and its unit cell contains four equivalent positions. The cell is stretched along the crystallographic b axis. Hereafter \( a \), \( b \), and \( c \) indicate crystallographic axes, whereas \( x_1 \), \( x_2 \), and \( x_3 \) designate the dielectric coor-
dinate system. Figure 2 shows projections of the crystal structure along the crystallographic $a$, $b$, and $c$ axes as well as the relation to the dielectric coordinate system. Note that the molecular packing of the crystal exhibits a $\Lambda$ shape [Fig. 2(c)], suggesting an optimized molecular packing for phase-matched second-harmonic generation and sum-frequency generation. The value of the angle between the charge-transfer axis (defined between the nitrogen atoms of the acceptor and the donor groups) and the dielectric polar axis $x_1$ is $\theta_{CT,1} = 50.6^\circ$, which is close to the optimum value of $\theta_{CT,1} = 54.7^\circ$ (Ref. 17); i.e., DANPH is a suitable candidate for second-harmonic generation and optical parametric oscillation when it is pumped in the near infrared (see the discussion below). Moreover, the molecular packing consists of $\Lambda$-shaped endless chains of hydrogen-bonded molecules along the [101] direction, where the interatomic distances between the atoms involved in the hydrogen bond [Figs. 1 and 2(a)] are, for N$_1$...O$_1$ and H...O$_1$, $d = 0.3122$ and $d = 0.2228$ nm, respectively. Between these chains there are only weak binding forces that lead to the growth of parallel platelets oriented perpendicular to $b$ that could be used for our optical investigations. Figures 2(a)–2(c) also reveal that a large anisotropy in the linear and nonlinear-optical properties can be expected: The refractive indices $n_1$ and $n_2$ are predicted to be large because there is a favorable projection of $x_1$ and $x_2$ along the charge-transfer axis of the DANPH molecules. $x_3$, however, is almost perpendicular to the charge-transfer axis, and therefore $n_3$ should be much smaller. According to the oriented gas model$^{17}$ and the same arguments, $d_{11}$ (and $r_{11}$) and especially $d_{33}$ should be large. On the other hand, the $\Lambda$ shape of DANPH will lead to smaller values of the diagonal elements of the electro-optic tensor than those of DAST.$^{13,14,18}$ Crystallographic $b$ plates with a size of 0.5 mm $\times$ 2 mm $\times$ 10 mm could be grown and were used for a first linear- and nonlinear-optical characterization.

3. LINEAR-OPTICAL PROPERTIES

The large optical anisotropy of DANPH, which is expected from the molecular packing of the crystal, is demonstrated by the anisotropy of the absorption coefficient. We measured the transmission of a 510-μm-thick unpolished sample ($b$ plate) with an ultraviolet–visible spectrometer (Perkin Elmer, Lambda 9). We calculated the absorption from the transmission measurements, taking into account multiple reflections from both surfaces (Fig. 3). Whereas the absorption cutoff (50% transmission) for light polarized along the dielectric $x_1$ axis is 700 nm, 50% transmission for light polarized along the dielectric $x_3$ axis occurs at $\lambda = 660$ nm. The anisotropy suggested...
The position of the optical axis (concentric interference plane-parallel surfaces of the crystal are perpendicular to measurement, confirming that the naturally growing angle on the crystal), smaller than the uncertainty in the agreement with the high nonlinearity of the DANPH molecule, the large value of the cutoff wavelength is in agreement with the high nonlinearity of the DANPH molecule.

The sample’s small minimum absorption at \( \lambda = 950 \text{ nm} \) (\( \alpha = 0.1 \text{ cm}^{-1} \)) reveals its good optical quality. The transmission of the crystal was measured up to a wavelength of \( \lambda = 10 \text{ \( \mu \)m} \) and revealed a strong but narrow absorption band near \( \lambda = 3.2 \text{ \( \mu \)m} \) and a cutoff near \( \lambda = 6 \text{ \( \mu \)m} \), emphasizing the potential of DANPH as a candidate for optical parametric oscillation pumped in the near infrared.

Inasmuch as DANPH crystallizes in point group \( m \), the index ellipsoid is only partly fixed with respect to the crystallographic coordinate system. The dielectric \( x_2 \) axis is always parallel to the crystallographic \( b \) axis, whereas the \( x_1 \) and \( x_3 \) axes are free to rotate with, \( \text{e.g.} \), the wavelength. Therefore we first measured the position of the index ellipsoid in relation to the crystallographic axes for different wavelengths. We found that the angles between the dielectric \( x_1 \) and \( x_3 \) axes and the crystallographic \( a \) and \( c \) axes are \( 23 \pm 2^\circ \) and \( 31 \pm 2^\circ \), respectively [Fig. 2(b)], and no rotation of the optical indicatrix around the \( b \) axis as a function of wavelength could be observed.

Using a conoscopic method fully described in Refs. 19 and 20, we measured the angle between the maximum phase difference, \( \text{i.e., the principal dielectric } x_2 \text{ axis and the direction } [010] \), perpendicular to the \( b \) axis. We found a value of less than \( 2^\circ \) (incidence angle on the crystal), smaller than the uncertainty in the measurement, confirming that the naturally growing plane-parallel surfaces of the crystal are perpendicular to the crystallographic \( b \) direction. We could not determine the position of the optical axis (concentric interference rings) experimentally by rotating the crystal because the angle between the optical axis and the crystallographic \( b \) axis is too large to be observed in the case of \( b \) plates.

With our small-sized first samples, an accurate determination of the refractive indices could be performed. Because the \( b \) planes were highly parallel, we chose a Mach–Zehnder interferometric method to determine the refractive indices in the range from \( \lambda = 700 \text{ nm} \) to \( \lambda = 1.3 \text{ \( \mu \)m} \). The crystals were mounted in one arm of the interferometer. We determined the refractive indices by rotating the crystal around an axis perpendicular to the laser beam and counting the number of interference fringes \( m \) that resulted from the change in the optical path length in one branch of the interferometer as a function of the angle of incidence \( \theta \). From \( m \) and \( \theta \) the refractive index \( n \) can be determined from the formula

\[
\frac{n}{n_1} = \frac{\alpha^2 + 2(1 - \cos \theta)(1 - \alpha)}{2(1 - \cos \theta - \alpha)}
\]

for \( s \)-polarized light and from

\[
m = \frac{2}{\lambda} L_s \left[ \frac{[n^2(\theta') - \sin^2(\theta)]^{1/2} - \cos \theta - \text{[n(0) - 1]}}{\sin^2 \theta'} \right]
\]

for \( p \)-polarized light, where \( \alpha = (m\lambda)/(2L_s) \), \( \lambda \) is the wavelength of the incident radiation, \( L_s \) is the sample thickness, \( \theta \) is the rotation angle away from normal incidence, \( \theta' \) is the internal angle of incidence, and \( n \) [and \( n(0) \)] is the refractive index of the sample.

The crystal was first rotated around the dielectric \( x_1 \) axis with light polarized parallel to the same axis \( (s\)-polarized light). By counting the fringes as a function of \( \theta \) we determined the optical path difference and therefore the refractive index \( n_1 \) [Eq. (1)]. We then changed the polarization of the beam to \( p \) polarization, thus measuring a combination of the two refractive indices \( n_2 \) and \( n_3 \) on crystal rotation. After determining \( n_3 \) in a way analogous to that for \( n_1 \) (rotating the crystal around the \( x_3 \) axis) with \( s \)-polarized light, we determined the value of \( n_2 \) from the measurement with \( p \)-polarized light and the knowledge of \( n_3 \) [Eq. (2)]. In addition, we determined \( n_2 \) by rotating the crystal around the main axis \( x_3 \), using \( p \)-polarized light. The two measurements yielded the same results for \( n_2 \), demonstrating the practicality of our method.

Table 1 shows the results together with the refractive indices evaluated from nonlinear-optical measurements made by the Maker-fringe method (see below). The experimental errors are due to the sample quality and not to the experimental method, which permits an accuracy of \( 2 \times 10^{-4} \) in the refractive index for a 0.5-mm-thick sample.

From the crystal structure of DANPH we could expect a very large anisotropy in the refractive indices, with \( n_1, n_2 \gg n_3 \). Figure 4 shows that such is indeed the case. A birefringence \( n_1 - n_3 \) of as much as 0.9 could be measured at \( \lambda = 700 \text{ nm} \). The dispersion of the refractive indices can be described by a Sellmeier oscillator function. If one oscillator with frequency \( \omega_0 \) dominates, the function is reduced to the form

\[
n^2(\omega) - 1 = A + \omega_p^2 \gamma / (\omega_p^2 - \omega^2),
\]

where \( \omega_p \) is the plasma frequency \( (\omega_p^2 = N e^2/m_0 e_0) \); \( N \) is oscillator density, \( e \) is the oscillator charge, \( m \) is the os-
for these parameters. The dispersion of this refractive index is too small to yield precise values for the Maker-fringe experiments discussed below.

### 4. NONLINEAR-OPTICAL PROPERTIES

We investigated the nonlinear-optical properties of DANPH, using small red needles (b plates). For a crystal with point group symmetry m the second-order nonlinear-optical susceptibility tensor has 10 nonzero components (d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, d_{26}, d_{31}, d_{32}, d_{33}, and d_{35}) expressed in the dielectric coordinate system, which result in the following macroscopic polarizations at frequency 2\omega:

\[
P_{1}^{2\omega} = \varepsilon_{0} d_{11} E_{1}^{2} + \varepsilon_{0} d_{12} E_{2}^{2} + \varepsilon_{0} d_{13} E_{3}^{2} + 2 \varepsilon_{0} d_{15} E_{1} E_{3},
\]

\[
P_{2}^{2\omega} = 2 \varepsilon_{0} d_{24} E_{2} E_{3} + 2 \varepsilon_{0} d_{16} E_{1} E_{2},
\]

\[
P_{3}^{2\omega} = \varepsilon_{0} d_{31} E_{1}^{2} + \varepsilon_{0} d_{32} E_{2}^{2} + \varepsilon_{0} d_{33} E_{3}^{2} + 2 \varepsilon_{0} d_{35} E_{1} E_{3}.
\]

Using the standard Maker-fringe technique, we measured several nonlinear-optical coefficients at \( \lambda = 1.907 \mu m \) and \( \lambda = 1.542 \mu m \) (first Stokes Raman shifts (H2 and CH4) of a Nd:YAG laser (wavelength \( \lambda = 1064 \text{ nm} \)), pulse duration \( \tau = 5 \text{ ns} \), repetition rate \( f = 10 \text{ Hz} \) (H2) or 2.5 Hz (CH4)). The plane-parallel sample was rotated around an axis perpendicular to the incoming laser beam and the frequency-doubled power measured with a photomultiplier. The signal was then processed with a boxcar (gated) integrator and recorded with a Macintosh computer by data acquisition. A quartz crystal (d_{11} = 0.4 pm/V) was used as a reference.

With our b plates we could directly determine the values of d_{11} and d_{33}. The large uncertainty in the measured value of d_{33} arises from the uncertainty in the corresponding coherence length because the refractive index \( n_3 \) shows almost no dispersion in the wavelength range above the absorption cutoff of the crystal. We could obtain the value of d_{32} (or d_{12}) by fitting the curve obtained by rotating the crystal around the dielectric x3 axis with incident in-plane polarized light (polarization in the x2-x3 plane, frequency \( \omega \)), detecting light at frequency 2\omega polarized in the x2-x3 plane (or detecting light polarized along the x1 axis for the determination of d_{12}). For perpendicular incidence the contribution from d_{32} (d_{12}) to the second-harmonic signal is zero. As the angle of incidence is increased, the contribution of d_{32} (d_{12}) becomes more and more important. Figure 5 shows the data obtained for the combination of d_{33} and d_{32} at \( \lambda = 1.542 \mu m \) for a 510-\mu m-thick DANPH sample along with a fit of our measured curves by use of a generalization of the model of Jerphagnon and Kurtz for the case of biaxial crystals. The second-order nonlinear-optical susceptibilities d_{12} and d_{32} are 270 and 35 pm/V, respectively. The values of d_{15} and d_{31} could not yet be determined with sufficient accuracy because of the small value of the corresponding coherence lengths compared with the surface roughness of the crystal. All measured values are listed in Table 2.

<table>
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<tr>
<th>( \lambda ) (nm)</th>
<th>( n_1 ) (±0.01)</th>
<th>( n_2 ) (±0.01)</th>
<th>( n_3 ) (±0.005)</th>
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<tr>
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<td>2.31</td>
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<tr>
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<td>2.02</td>
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<tr>
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<td>2.00</td>
<td>2.00</td>
<td>1.445</td>
</tr>
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</table>

**Sellmeier Parameters**

\( \omega_{eg} \) (10^{15} \text{ s}^{-1}) = 3.586, 3.880, 13.625

\( d_{eg} \) (nm) = 525.6, 485.8, 138.4

\( \gamma_{0} \omega_{eg}^2 \) (10^{30} \text{ s}^{-1}) = 16.06, 22.42, 161.84

A = 1.652, 1.376, 0.215

*Values indicated by asterisks were calculated from the coherence lengths of Maker-fringe measurements. The parameters used to fit the refractive indices with a one-oscillator Sellmeier model are also listed. The Sellmeier parameters obtained for \( n_3 \) are only approximate because the dispersion of this refractive index is too small in the transparency range of the crystal. This fact led to uncertainties in the calculation of the coherence lengths for light propagating along the dielectric x3 axis that are important for the Maker-fringe experiments discussed below.
about the correct values to be used for the Sellmeier curve was used. Note that there is still an uncertainty in the coherence length could not be measured, the corresponding value obtained instead, all our results in this table become 25% smaller.

Table 1, the values of the refractive index above 1.9

<table>
<thead>
<tr>
<th>(i)</th>
<th>d_{ij} (pm/V)</th>
<th>l_{ij} (μm)</th>
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<tr>
<td>11</td>
<td>185</td>
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<tr>
<td>33</td>
<td>0.1</td>
<td>51</td>
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<tr>
<td>12</td>
<td>260</td>
<td>1.67</td>
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<tr>
<td>32</td>
<td>21</td>
<td>0.7</td>
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λ=1542 nm

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<th>d_{ij} (pm/V)</th>
<th>l_{ij} (μm)</th>
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<tr>
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λ=1907 nm

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<td>4.0</td>
</tr>
<tr>
<td>32</td>
<td>15</td>
<td>0.9</td>
</tr>
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</table>

Values indicated by asterisks are the values calculated from Maker-fringe experiments according to Jerphagnon and Kurtz. When the coherence length could not be measured, the corresponding value obtained by the Sellmeier curve was used. Note that there is still an uncertainty about the correct values to be used for d_{11} of quartz. Here we used d_{11} = 0.4 pm/V. If the suggested value of d_{11} = 0.3 pm/V (Ref. 24) is used instead, all our results in this table become 25% smaller.

5. PHASE-MATCHING CONSIDERATIONS

The Λ-shaped molecular packing of DANPH suggests an ideal configuration for phase-matched second-harmonic generation, sum-frequency generation, and optical parametric oscillation. Using the Sellmeier parameters listed in Table 1 (the values for the monomeric index above 1.9 μm are calculated with Eq. (3) and the parameters of Table 1), we calculated the directions of the wave vectors in the crystal for which the phase-matching conditions for second-harmonic generation or sum-frequency mixing are satisfied for collinear interaction.

For phase-matched parametric interactions among three waves, where ω_3 = ω_1 + ω_2, the interacting waves must satisfy k_3 = k_1 + k_2. That is, in the case of collinear interaction, if all the k_i are parallel to one another, then n_{ω_3}k_3 = n_{ω_1}k_1 + n_{ω_2}k_2, where n_{ω_j} are the refractive indices for the waves at frequencies ω_j. For general directions of the wave vectors and polarizations in the crystal the induced nonlinear polarization at ω_j can be written as

\[
|P|^{ω_j} = 2\varepsilon_0|P|^2_{eff}|E|^{ω_j} (type II),
\]

\[
|P|^{2ω} = \varepsilon_0|P|^2_{eff}|E|^2 (type I)
\]

for second-harmonic generation with the effective nonlinear-optical coefficient

\[
d_{eff} = \sum_{ijk} d_{ijk}(ω_3, ω_1, ω_2)\cos(α_{ω_3})\cos(α_{ω_1})\cos(α_{ω_2}),
\]

where α_{ω} is the angle between the electric-field vector of the wave ω and the main axis i of the indicatrix. Note that we took the walk-off angle into account to calculate the angles α_{ω}.

Figure 6 shows the propagation directions (expressed in spherical coordinates Φ and Θ [Fig. 7(a)]) for which phase-matched second-harmonic generation (types I and II) occurs in a DANPH crystal at λ = 1.542 μm. Because of the large birefringence of DANPH (n_3 < n_1, n_2), non-critical phase matching cannot be achieved along a main axis of the indicatrix, and a rotation of the crystal around its x_3 axis leads only to a small change in the phase-matching wavelengths. The optimum phase-matching condition for second-harmonic generation at λ = 1.542 μm in DANPH was found for type I phase matching and for a propagation direction of Φ = 0° and Θ = 24.7°, leading to an effective nonlinear-optical coefficient larger than 150 pm/V (Fig. 7). For the calculation of the effective nonlinear-optical coefficients for second-harmonic generation at 1.542 μm we used the measured values (Table 2) and approximated the missing coefficients through calculations based on the oriented gas model.
As is discussed below, this is a valid procedure. For this configuration the walk-off angle was found to be larger than 20°, which is not desirable for application in optical parametric oscillation but nevertheless can be compensated for by use of noncollinear configurations.\textsuperscript{27,28}

Figure 7(b) shows the main contributions to $d_{eff}$ for type I phase-matched second-harmonic generation at 1.542 µm in DANPH [including the projection factors of Eqs. (5)]. The highest value for the effective nonlinear-optical coefficient, $d_{eff} = 157$ pm/V, is due to a favorable combination of $d_{12}$ and $d_{32}$.

Phase-matched sum-frequency generation or optical parametric oscillation can occur for several propagation directions in a DANPH crystal. Figure 8 shows the possible configurations for different propagation directions for types I and II. When a DANPH crystal is rotated around its $x_1$ or $x_2$ axis, light can be generated over a wide range of wavelengths (from 1 to 4 µm) through optical parametric oscillation. With a Ti:sapphire pump laser (with $\lambda_3 = 800$ nm) light can be generated over the whole wavelength range by angle tuning around the $x_2$ axis with
tuning angles $\Theta$ between 20° and 24°, which corresponds to an external angular tuning range of the crystal of ~11° for a c plate. For a Nd:YAG pump laser (with $\lambda_3 = 1.064 \mu m$) angle tuning around the $x_3$ axis with $\Theta$ between 14° and 17° can be used, leading to an external angular tuning range of the crystal of ~7° for a c plate. Phase-matched sum-frequency generation or optical parametric oscillation can also be achieved with a tunable pump laser for a fixed propagation direction in the crystal (Fig. 9). With a Ti:sapphire pump laser and its tuning range between 800- and 900-nm light can be generated from 1 to 4 $\mu m$ with a fixed propagation direction of $\Phi = 0°$ and $\Theta = 20°$ in DANPH.

6. DISCUSSION AND CONCLUSION

With the charge-transfer axis defined between the nitrogen atoms of the acceptor and donor groups, the angles between this axis and the dielectric axes $x_1$, $x_2$, and $x_3$ of the crystal were calculated: $\theta_{CT,1} = 50.6°$, $\theta_{CT,2} = 39.8°$, and $\theta_{CT,3} = 85.2°$. Using the measured value $\beta_{zzz} = 200 \times 10^{-40} m^4/V$ at $\lambda = 1.907 \mu m$ ($\lambda_0 = 420 nm$ in 1,4-dioxane), the number density of the molecules in the crystal $N = 2.727 \times 10^{27} m^{-3}$, a local-field correction of ~10, and the oriented gas model, we estimated the second-order nonlinear-optical coefficients $d_{11}$, $d_{12}$, $d_{32}$, and $d_{33}$ at $\lambda = 1.907 \mu m$ (see, e.g., Ref. 20 for a description of such calculations). Using the above value of $\beta$ at $\lambda = 1.907 \mu m$, we calculated a hyperpolarizability $\beta_{zzz} = 273 \times 10^{-40} m^4/V$ at $\lambda = 1.542 \mu m$ from the two-level model. We used this value to estimate $d_{11}$, $d_{12}$, $d_{32}$, and $d_{33}$ at the corresponding wavelength (Table 2). This simple approximation gives values in good agreement with the experimental data, which is rather surprising because it is quite difficult to determine precisely the charge-transfer axis of the DANPH molecules that are bent in the crystal lattice. The good agreement also shows the validity of our approach for the determination of the phase-matchable effective nonlinear coefficients $d_{eff}$.

We can also compare the same nonlinear-optical susceptibilities at different wavelengths. The quantum-mechanical two-level model predicts that

$$d_{11}^{1542} = 1.5, \quad d_{12}^{1542} = 1.5,$$

which compare reasonably well with our measurements within the experimental error:

$$d_{11}^{1542} = 1.4, \quad d_{12}^{1542} = 1.7.$$

DANPH shows one of the largest nonlinear-optical coefficients in the near infrared and, to the best of our knowledge, the largest phase-matchable coefficient in a bulk material, namely, $d_{21} = 270 \pm 50 pm/V$ at $\lambda = 1.542 \mu m$, and the corresponding effective nonlinear-optical phase-matchable coefficient $d_{eff} \approx 150 pm/V$ at $\lambda = 1.542 \mu m$. The large values reported here make DANPH an interesting material for cascaded second-order nonlinearities for enhanced third-order nonlinear-optical response, optical parametric oscillation in the near infrared or for both. We can compare the nonlinearity of DANPH with that of other materials by introducing $d_{max}$ which is the maximum nonlinear-optical coefficient, assuming a perfect molecular alignment:

$$d_{ijk} = d_{max} \cos(\theta_{CT,i}) \cos(\theta_{CT,j}) \cos(\theta_{CT,k}).$$

First we can compare the projection factors. For the phase-matched coefficient $d_{12}$ we get $d_{12} = d_{max} \max \times \cos(50.6°) \times \cos(39.8°) = 0.375 \times d_{max}$. For the optimized Cc structure we get $d_{ij} = d_{max} \times \cos(54.7°) \times \sin(54.7°) = 0.385 \times d_{max}$. This is, the orientation of the DANPH molecules in the crystal lattice is almost ideal for phase-matched second-harmonic generation and optical parametric oscillation.

The value of $d_{max}$ for DANPH ($d_{max} = 780 pm/V$) is comparable with the corresponding one for DAST ($d_{max} = 1000 $ pm/V), both at $\lambda = 1.542 \mu m$. Because of the different $\theta_{CT,i}$, however, DAST is optimized for electro-optics, whereas DANPH is most suitable for frequency mixing. Moreover, the figure of merit $d^2\rho^3$ for second-harmonic generation of DANPH, which is directly proportional to the conversion efficiency, compares favorably (1-2 orders of magnitude larger) with those of the best inorganic and organic single crystals (Table 3). Notice that the values of the other compounds listed in the Table 3 were given at $\lambda = 1.064 \mu m$ and are significantly smaller at $\lambda = 1.542 \mu m$.

We calculated the electronic contribution to the electro-optic coefficients $r_{ij}$ from our measured nonlinear-optical susceptibilities $d_{ij}$, using well-known equations for the wavelength dispersion and the relation between $r_{ij}$ and $d_{ij}$. These calculations give values of $d_{11} = 26 pm/V$ and $d_{21} = 54 pm/V$ at $\lambda = 1.542 \mu m$ and of $d_{11} = 47 pm/V$ and $d_{21} = 67 pm/V$ at $\lambda = 800 nm$ that are also interesting.

In conclusion, we have evaluated the linear- and nonlinear-optical properties of a new organic single crystal, DANPH. We have shown that this material has interesting properties for phase-matched nonlinear-optical interactions such as cascading of second-order nonlineari-
ties and optic parametric oscillation. DANPH is just one of the promising materials based on the hydrazone backbone. Other derivatives with improved nonlinear-optical properties are likely to be found in the near future.

ACKNOWLEDGMENTS
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REFERENCES
28. S. X. Dou, D. Joesse, and J. Zyss, “Comparison of collinear and one-beam noncritical noncollinear phase matching in

Table 3. Comparison of the Figure of Merit for Type I Phase-Matched Second-Harmonic Generation of Some Inorganic and Organic Single Crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavelength (nm)</th>
<th>$d_{21}^2$ [pm/V]^2</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DANPH</td>
<td>1542</td>
<td>3065</td>
<td>This work</td>
</tr>
<tr>
<td>N-(4-nitrophenyl)-(L)-prolinol (NPP)</td>
<td>1064</td>
<td>834*</td>
<td>36</td>
</tr>
<tr>
<td>DAN [4-(N,N-dimethylamo)-3-acetamidino-nitrobenzene]</td>
<td>1064</td>
<td>125</td>
<td>37</td>
</tr>
<tr>
<td>2-(N-prolinol)-</td>
<td>1064</td>
<td>83</td>
<td>38, 39</td>
</tr>
<tr>
<td>5-nitropyridine (PNP)</td>
<td>722*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>860</td>
<td>40*</td>
<td>40</td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>1064</td>
<td>2.6</td>
<td>40</td>
</tr>
</tbody>
</table>

*Note that all values except for NPP [reference, $d_{11}^{(1)}$ (quartz)] 0.5 pm/V correspond to a reference of $d_{11}^{(1)}$ (quartz) 0.4 pm/V to permit a meaningful comparison. The values indicated by asterisks correspond to nontypical phase matching.