

Dual Influence of H-Bonding on the Solid-State Second-Harmonic Generation of a Chiral Quinonoid Compound

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A new chiral push–pull quinonoid compound, 7,7-bis(3(*R*)-hydroxypyrrolidino)-8,8-dicyanoquinodimethane (BHPDQ), has been synthesized. Powder studies indicate an appreciable second harmonic generation (SHG) capability, and crystal structure analysis reveals extensive intermolecular H-bonding in BHPDQ. The influence of H-bonding and molecular chirality on the dipole alignment in the crystal is described. The H-bonds play an unusual role of modifying the molecular structure by producing an enhanced molecular twist in BHPDQ; this in turn affects the molecular hyperpolarizability. Thus we describe a novel instance wherein the powder SHG in a molecular material is determined by the dual influence of intermolecular H-bonding on the crystal structure as well as on the molecular structure and hyperpolarizability. The new dimension that this observation adds to the general theme of molecular materials design is highlighted.

Introduction

Molecular materials based on organic and organometallic compounds afford great flexibility in the design of the crystal architecture through the manipulation of a wide range of subtle features such as chirality, steric factors, H-bonding, and π -stacking. Such control on the solid-state structure is crucial to the design of noncentrosymmetric crystal lattices which are essential for quadratic nonlinear optical (NLO) applications.¹ Further, these crystal design techniques can be exploited to achieve optimal packing of the molecular NLO chromophores so that the bulk nonlinear susceptibilities are enhanced.² At the molecular level, the hyperpolarizabilities can be increased by appropriate structural modifications. In recent years, molecular materials have emerged as some of the most promising candidates for NLO applications such as second harmonic generation (SHG).³

H-bonding is one of the most effective and popular tools for the design of crystal structures.⁴ Urea is one of the finest examples of simple molecular structural units forming a three-dimensional crystalline network involving an efficient utilization of extensive H-bond-

ing.⁵ Among the multiple options available for the molecular packing which satisfy the strong dipolar forces, the one which simultaneously maximizes the H-bonding interactions is found in the urea crystal. This leads to a concomitant breaking of the center of symmetry and SHG capability. H-bonding is often utilized together with other features such as chirality⁶ and steric factors⁷ to achieve optimal alignment of NLO chromophores and high SHG capability in the bulk material. An illustrative case is *N*-(4-nitrophenyl)-*L*-prolinol (NPP).^{6b} The chirality in the prolinol unit ensures the noncentrosymmetry of the lattice and the H-bonding leads to a crystal packing wherein the molecular dipole alignment is close to the optimal for SHG. Weak to moderate SHG capability has been achieved in crystals having extensive H-bonding with^{8–10} or without¹¹ sup-

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port from chirality to induce the noncentricity. Most of the earlier studies have focused on the influence of H-bonding on the crystal packing. The impact of H-bonding on the molecular structure and hence on the molecular hyperpolarizability that has a direct bearing on the crystal NLO properties has generally been less significant and less attention has been paid to it. However a theoretical investigation of the effect of H-bonding on the hyperpolarizabilities of molecular dimers has been reported.¹²

Recently we have developed a new class of NLO chromophores based on substituted diaminodicyanoquinodimethanes, first reported by du Pont investigators.¹³ The new chiral derivatives we have synthesized show moderate to high SHG capability^{14,15} and an achiral derivative shows an interesting case of solvate-switchable powder SHG.¹⁶ In an effort to investigate the implications of extended H-bonding interactions on these push-pull quinonoid systems, we have now synthesized a new chiral NLO material, 7,7-bis[3(*R*)-hydroxypyrrolidino]-8,8-dicyanoquinodimethane (BHPDQ). Crystal structure analysis indicated extensive intermolecular H-bonding involving the hydroxyl groups and one of the cyano groups in the molecule. The appreciable SHG of 13 U (1 U = SHG of urea) is observed in this material. We have observed earlier¹⁵ that the placement of the stereogenic center on the rigid framework of a cyclic side group leads to strong deviations of the molecular dipoles from an antiparallel alignment. This seems to be borne out in the present material as well. The H-bonding interactions assist in this molecular packing and hence contribute positively to the bulk SHG. However, we noticed an unusual effect of the intermolecular H-bonding in this crystal in terms of enhancing the molecular twist found in this class of zwitterionic push-pull systems. This molecular structural change leads to a diminished oscillator strength for the lowest energy excitation and a decrease in the hyperpolarizability; the latter effect has a negative impact on the bulk SHG, whereas the former has a positive influence in terms of improving the transparency window of this material. Thus we present an interesting case of the dual influence of H-bonding on the crystal and molecular structures of a push-pull quinonoid molecular material and hence on its NLO property. The significance of this observation to the larger context of molecular materials design is highlighted. We have also investigated the relevance of chirality to the SHG capability of BHPDQ.

Experimental Section

Synthesis of 7,7-Bis[3(*R*)-hydroxypyrrolidino]-8,8-dicyanoquinodimethane (BHPDQ). The method reported in ref 13 was adopted. To a warm solution of 0.10 g (0.49 mmol) of TCNQ in 50 mL of THF was added 0.17 g (1.96 mmol) of 3(*R*)-hydroxypyrrolidine (**CAUTION:** HCN gas is evolved in this reaction). A dark green color developed immediately. The

solution was stirred for 2.5 h at 50 °C. The color faded and a yellow precipitate appeared. The reaction mixture was cooled to 5 °C and the precipitate filtered out. The filter cake was washed first with cold THF and then with cold ether to give 0.137 g of cream-colored BHPDQ (86% yield). It was recrystallized from methanol: mp 260 °C (dec); FTIR (KBr wafer) $\bar{\nu}/\text{cm}^{-1}$ 3375 (O-H stretch), 2184, 2137 (conjugated nitrile stretch); UV-vis (acetonitrile solution) $\lambda_{\text{max}}/\text{nm}$ 388; $[\alpha]_{\text{D}}^{25}$ -175° ($c = 0.03$, MeOH); FAB mass (m/z) 325 ($M + 1^+$), 324 (M^+), 154. Elemental analysis, % found (% calculated for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_2$): C, 66.90 (66.66); H, 6.16 (6.17); N, 17.44 (17.28).

Synthesis of 7,7-Bis[3-hydroxypyrrolidino]-8,8-dicyanoquinodimethane from Racemic 3-Hydroxypyrrolidine. The compound from racemic 3-hydroxypyrrolidine was prepared in a similar way as above and recrystallized from methanol: mp 265 °C (dec); FTIR (KBr wafer) $\bar{\nu}/\text{cm}^{-1}$ 3375 (O-H stretch), 2174, 2131 (conjugated nitrile stretch); UV-vis (acetonitrile solution) $\lambda_{\text{max}}/\text{nm}$ 393; $[\alpha]_{\text{D}}^{25}$ 0° ($c = 0.03$, MeOH); FAB mass (m/z) 325 ($M + 1^+$), 324 (M^+), 185. Elemental analysis, % found (% calculated for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_2$): C, 66.48 (66.66); H, 6.34 (6.17); N, 17.16 (17.28).

Powder SHG Studies. The powder SHG measurements were carried out using the Kurtz-Perry method.¹⁷ The fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser (Continuum, Model 660B-10) was used. The detection system consisted of a photomultiplier tube (Hamamatsu), oscilloscope (Tektronix, Model 2465B, 400 MHz) or lock-in amplifier (SRS, Model SR830), and personal computer. Powder samples were sandwiched between glass plates with the thickness of the sample controlled by 200 μm thick uniform Teflon sheets. Powder sizes were graded using standard sieves. Urea (particle size 100–150 μm) and NPP (particle size 250–300 μm) were used as standards. All the materials we have investigated have shown very good stability under laser irradiation and no sign of decomposition even on continued irradiation with a laser power of 1 GW/cm^2 (6 ns, 10 Hz) was detected. The error associated with the powder SHG measurements is typically about 15%.

Theoretical. All the computations were carried out using the MOPAC93¹⁸ suite of programs. Geometry optimizations were carried out using the AM1¹⁹ procedure imposing the PRECISE option; constraints if applied, are mentioned at the appropriate places. Hyperpolarizabilities were calculated using the CPHF method^{3b} implemented in MOPAC93. The hyperpolarizabilities reported are the averaged values at zero excitation energies, $\beta_{\text{av}}(0)$; for convenience this is denoted simply as β .

Results and Discussion

Our earlier studies have indicated that substituted diaminodicyanoquinodimethane molecules have large hyperpolarizabilities,^{15,20} in agreement with the EFISHG investigation of a prototypical system by Lalama et al.²¹ and our own recent experiments.²² These molecules have relatively high absorption energies with λ_{max} typically between 370 and 400 nm; hence, they are of potential interest in visible light NLO applications. The zwitterionic nature of these compounds leads to strong electrostatic interactions in the crystalline state and relatively high melting points, typically > 250 °C; most of the well-known NLO molecular crystals melt below 150 °C.²³ The thermal stability and resistance to

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degradation under laser irradiation are extremely important from an application point of view. The zwitterionic nature of these molecules leads also to large ground-state dipole moments of the order of 10–15 D. Correlation between dipole moments of molecules and the tendency to form centrosymmetric crystal lattices has been questioned;²⁴ however, in these systems the large dipole moments appear to promote centrosymmetric crystal structures.²⁵ We have overcome this problem by using the sole effect of molecular chirality to produce materials which showed moderate (3 U) to strong (55 U) phase-matchable SHG. In these materials we were mainly interested in examining the role of the stereogenic center in steering the molecular dipole alignment.

We have now investigated the effect of intermolecular H-bonding on the solid-state structure and NLO properties of these quinonoid systems. The simplest functionalization of the molecular structure for this purpose is the introduction of hydroxyl groups on the amine donor moiety. Even though double substitution on TCNQ by 2-amino alcohols is reported,¹³ the reaction of prolinol with TCNQ led to intractable products.²⁶ Similar difficulties were encountered with valinol. Reaction of prolinol with 7-pyrrolidino-7,8,8-tricyanoquinodimethane was also unsuccessful. Since we suspected the interference from the adjacent hydroxy group in all these reactions, we chose to introduce 3(*R*)-hydroxypyrrolidine. The basic pyrrolidine skeleton would facilitate comparison of the new material to our earlier systems such as 7,7-dipyrrolidino-8,8-dicyanoquinodimethane (DPDQ)¹⁶ and 7,7-bis(2-*S*-methoxymethylpyrrolidino)-8,8-dicyanoquinodimethane (DMPDQ).¹⁵ We have now synthesized the bis-(3(*R*)-hydroxypyrrolidino)-substituted compound, BHPDQ, as well as the compound from racemic 3-hydroxypyrrolidine.

BHPDQ gave crystals suitable for structure determination from an acetonitrile–methanol mixture. Single-crystal structure analysis indicated the $P2_12_12_1$ space group (Table 1). The molecular structure is depicted in Figure 1. Important bond lengths, angles, and dihedrals are collected in Table 2. The bond lengths in the benzenoid ring are found to be quite similar to those found in the crystals of DPDQ, DMPDQ, and related compounds and indicates the zwitterionic nature arising as a result of the strong electron-donating and -accepting groups present. The novel and significant feature that this structure displayed is the high twist angle of 73.8° between the benzenoid plane and the plane containing the diaminomethylene unit (θ in Figure 1). A smaller twist angle in the range 43–58° is found in the seven crystals of these push–pull quinonoid compounds studied earlier;¹⁵ this twist may be attributed to the steric repulsions between the H atoms on the neighboring carbon atoms of the amino N's and the ortho H atoms on the benzenoid ring. The clearly enhanced θ in the case of BHPDQ is therefore considered significant and we analyze its origin and implications below. This structure also showed a modest twist

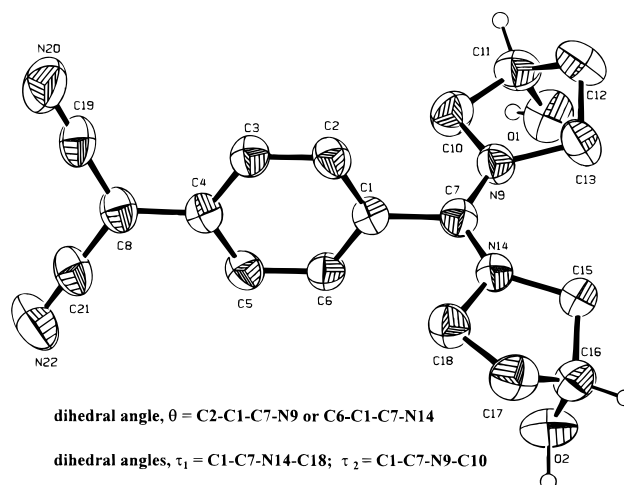


Figure 1. Molecular structure of BHPDQ from single-crystal X-ray analysis. H atoms of only the stereogenic centers and the hydroxyl groups are shown; 50% thermal ellipsoids are indicated. Definition of the dihedral angles θ and τ are noted.

Table 1. Crystallographic Data for BHPDQ

molecular formula	$C_{18}H_{20}N_4O_2$
morphology	plates
crystal system	orthorhombic
space group	$P2_12_12_1$
a, Å	11.761(3)
b, Å	16.888(2)
c, Å	8.537(1)
α, β, γ , deg.	90.0
V, Å ³	1695.6(6)
Z	4
ρ_{calcd} , g cm ⁻³	1.27
$\mu(\text{Cu K}\alpha)$, cm ⁻¹	6.55
no. of unique reflections	1754
no. of reflections with $I \geq 2\sigma_I$	1584
no. of variables	218
R	0.037
R_w	0.053

of the dicyanomethylene unit out of the benzenoid ring plane; such a twist has not been observed in the earlier structures in this series.

Figure 2 shows the stereoview of the unit cell along the *c* axis. As noted earlier, the stereogenic center on the rigid ring has been effective in inducing strong deviation from an antiparallel alignment of the molecular dipoles. The search for short intermolecular contacts revealed four well-defined H-bonds connecting each molecule to its neighbors; there are no intramolecular H-bonds. One of the hydroxyl groups [O(1)] acts solely as a H-bond donor, leading to the O(1)–H···O(2') bond. The other hydroxyl group [O(2)] acts as a H-bond donor as well as an acceptor leading to the O(2)–H···N(22') and O(2)···H–O(1') bonds; N(22) is the N atom of one of the cyano groups. The fourth bond is N(22)–···H–O(2). The H-bond links between the oxygen atoms leads to a zigzag chain extending roughly along the *a* direction (Figure 3a) and the H-bonds between the oxygen atom and the nitrogen atom give rise to a zigzag chain extending approximately along the *b* axis (Figure 3b). These H-bonds form an extended network in the *ab* plane.

The BHPDQ molecule is thus tied down by four H-bonds. It appears that these four intermolecular interactions in the solid state are accommodated at the cost of the increased dihedral twist (θ) of the molecule

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Table 2. Significant Bond Lengths and Bond and Dihedral Angles in BHPDQ from Single-Crystal X-ray Analysis and from the AM1 Computation^a

	CS	AM1
distance (Å)		
C(1)–C(2)	1.383(3)	1.415
C(1)–C(6)	1.389(3)	1.415
C(1)–C(7)	1.485(3)	1.462
C(2)–C(3)	1.380(3)	1.368
C(3)–C(4)	1.411(3)	1.436
C(4)–C(5)	1.395(3)	1.436
C(4)–C(8)	1.444(3)	1.387
C(5)–C(6)	1.376(3)	1.368
C(7)–N(9)	1.321(3)	1.365
C(7)–N(14)	1.322(3)	1.365
C(8)–C(19)	1.404(4)	1.412
C(8)–C(21)	1.381(4)	1.412
C(19)–N(20)	1.148(4)	1.166
C(21)–N(22)	1.158(4)	1.166
angle (deg)		
C(1)–C(7)–N(9)	118.1(2)	118.5
C(1)–C(7)–N(14)	117.3(2)	118.3
C(7)–N(9)–C(10)	121.3(2)	120.7
C(7)–N(9)–C(13)	128.7(2)	127.4
C(7)–N(14)–C(18)	121.9(2)	120.7
C(7)–N(14)–C(15)	127.3(2)	127.4
N(9)–C(7)–N(14)	124.6(2)	123.2
C(10)–N(9)–C(13)	109.9(2)	111.6
C(15)–N(14)–C(18)	110.4(2)	111.5
C(1)–C(7)–N(9)–C(10)	12.1(3)	12.1 ^b
C(1)–C(7)–N(14)–C(18)	5.6(3)	5.6 ^b
C(2)–C(1)–C(7)–N(9)	73.9(3)	73.9 ^b
C(3)–C(4)–C(8)–C(19)	17.5(3)	0.0
C(5)–C(4)–C(8)–C(21)	11.9(4)	0.2
C(6)–C(1)–C(7)–N(14)	73.7(3)	73.7 ^b

^a The atom labeling is shown in Figure 1. ^b The θ and τ angles are fixed (see text for details).

since this angle is 15–30° lower in the non-H-bonded systems of this series investigated earlier. Further support for this comes from our computational studies. Earlier semiempirical AM1 optimizations have shown that the twist angles in these substituted diaminodicyanoquinodimethanes are in the range 40–58°; the molecular structures from single-crystal analysis also showed very similar twist angles.¹⁵ In the case of BHPDQ, complete geometry optimization indicated a dihedral twist of 56.4°; this is likely to be the twist angle in its gas-phase structure and the enhancement of about 17° in the crystal appears to be a consequence of the environment and interactions in the crystalline state. We analyze this further using AM1 computations.

The following calculations were carried out using the molecular structure from single-crystal analysis as the starting point. First we fixed all the geometry parameters except the dihedral angle (θ) (a pseudo C_2 symmetry with respect to this dihedral angle was assumed; otherwise unphysical distortions of the molecule occur) and carried out calculations by varying θ in steps of 2° from 0 to 90°. The enthalpy of formation as a function of θ is plotted in Figure 4a. Though the potential energy surface is relatively flat after 60°, there is a clear minimum at 66° (inset of Figure 4a); this is about 8° less than that found in the crystal. Next we have carried out a similar calculation by varying the dihedral angles τ_1 and τ_2 (Figure 1) through 180° in steps of 6° each, keeping all other geometric parameters fixed. The enthalpies of formation are plotted in Figure 4b. The global minimum on this surface corresponds to $\tau_1 = 6^\circ$ and $\tau_2 = 6^\circ$, close to the values found in the crystal

structure (5.6° and 12.1°, respectively), indicating that the crystal forces do not cause any significant rotation of the pyrrolidine rings. Finally we have kept the θ and τ angles in the crystal molecular geometry fixed and allowed complete optimization of the rest of the geometry. The optimized bond lengths and angles are provided in Table 2. It is seen that the molecule is strongly benzenoid in the crystal and develops a more quinonoid structure upon geometry optimization; we note that the complete optimization, relaxing the θ and τ angles as well, leads to an even more quinonoid structure. The benzenoid structure owes its origin to the strong electrostatic environment present in the crystal, which promotes the zwitterionic form. These stepwise computations reveal that the quinonoid to benzenoid transformation of the six-membered ring and the enhancement of the twist angle are coupled and arise as a result of the combined influence of the electrostatic crystal environment and intermolecular H-bonding. The more benzenoid form in the crystal is familiar in the earlier systems;¹⁵ however, the enhanced twist angle appears to have been triggered by the intermolecular H-bonds in BHPDQ. The twist of the dicyanomethylene group observed in the crystal (compare the relevant dihedral angles in Table 2) also results from the intermolecular H-bonding.

In a computational study of DPDQ,¹⁵ we have observed that the energy (ΔE) and oscillator strength of the first excited state are affected by the extent of the dihedral twist, θ . When θ increases from 54° to 72°, the ΔE increases marginally, but the oscillator strength decreases by more than 50%. Experimentally, the solution absorption spectrum of BHPDQ and other systems are very similar; for example, the λ_{\max} values for BHPDQ and DPDQ in acetonitrile are respectively 388 and 375 nm. This indicates that the twist angle of BHPDQ in solution is similar to that in the other compounds. The absorption spectra of BHPDQ and DPDQ in thin KBr wafers were recorded and both showed absorption maximum at 360 nm; the increase of ΔE from solution to the solid-state results from the stabilization of the zwitterionic ground state in the more polar crystal environment. The increased molecular twist of BHPDQ has not led to any observable change in its ΔE with respect to the other systems such as DPDQ. However, for the same concentrations of BHPDQ and DPDQ, the absorbance values at λ_{\max} are approximately in the ratio 1:3, resulting in λ_{cutoff} of 521.5 and 553.8 nm, respectively. This is consistent with the light yellow color of DPDQ and other non-H-bonded systems and the distinctly lighter cream color of BHPDQ. We infer that the enhanced twist angle of BHPDQ has led to the reduced oscillator strength of its lowest energy excitation. Thus the H-bond tethers which have modified the molecular structure have contributed to an improved transparency for this material in the visible range.

The focus of the computational study of DPDQ¹⁵ was the strong dependence of hyperpolarizability (β) on the twist angle (θ). It was found that the β went through a maximum at $\theta \sim 55^\circ$ and decreased by approximately 40% at $\theta \sim 70^\circ$. The β values calculated for DPDQ and other systems using the molecular geometry from

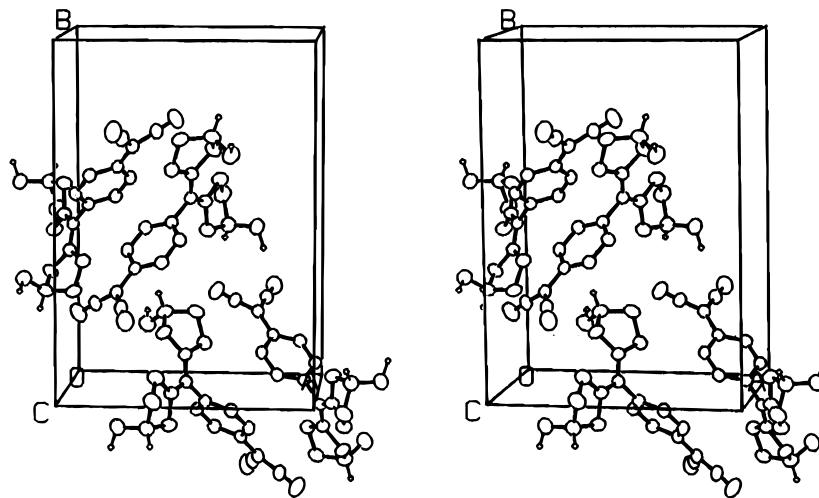


Figure 2. Stereoview of the unit cell (from single-crystal X-ray analysis) of BHPDQ along the *c* axis.

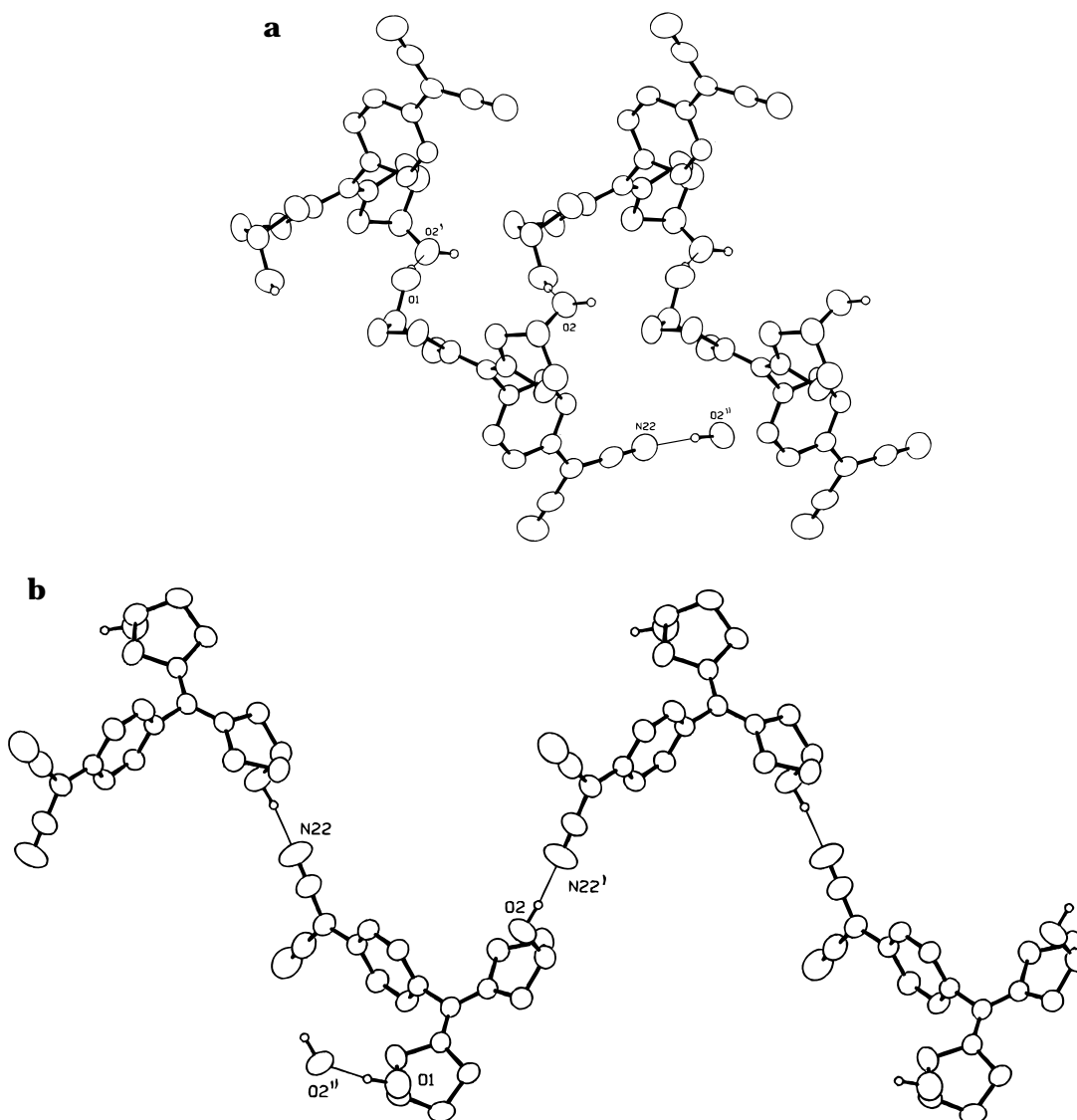


Figure 3. H-bonded chains in BHPDQ (a) along the *a* axis [$O1-H\cdots O2'$; $r_{H\cdots O} = 1.69(1)$ Å, $\angle O-H\cdots O = 171(1)^\circ$] and (b) along the *b* axis [$O2-H\cdots N22'$; $r_{H\cdots N} = 1.75(1)$ Å, $\angle O-H\cdots N = 171(1)^\circ$]; the H-bonds are shown using thin lines.

crystal structure analysis are in the range -50 to -54×10^{-30} esu; the corresponding value for BHPDQ is -31.3×10^{-30} esu. The decrease in β due to the enhanced twist is quite consistent with the trend

predicted earlier. Thus the strong modification of the molecular structure of BHPDQ brought about by the H-bond matrix has contributed negatively to the molecular hyperpolarizability.

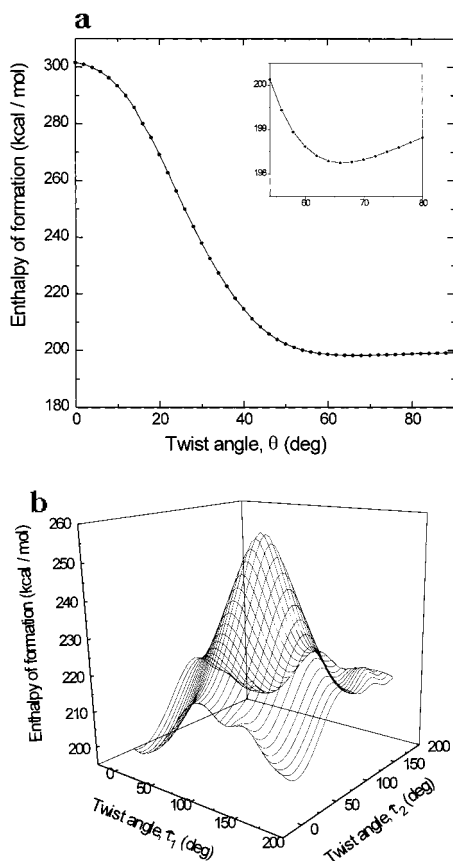


Figure 4. Plot of the computed (AM1) enthalpy of formation of BHPDQ as a function of (a) twist angle θ (the inset shows the valley clearly) and (b) the dihedral angles τ_1 and τ_2 ; see text for details of the computation and Figure 1 for the definition of the dihedral angles.

The quinonoid–benzenoid character of the molecule exerts a strong influence on the hyperpolarizability as shown by model calculations on 7,7-diamino-8,8-dicyanoquinodimethane.²⁰ The quinonoid–benzenoid nature was quantified using a parameter called QBC, which ranges from 0 to 1 as the structure evolves from a fully quinonoid state to a fully benzenoid state. It was found that β calculated in the absence of applied fields increased almost linearly with the QBC. As a consequence, β calculated using the AM1-optimized structures are usually smaller (in the range -20 to -40×10^{-30} esu) than the values calculated using the molecular structure from the single-crystal analysis, which are more benzenoid, as shown above. However, in the case of BHPDQ, β calculated using the optimized AM1 geometry, -30.4×10^{-30} esu, is nearly the same as the value calculated for the experimental molecular structure, even though the molecule is clearly more benzenoid in the crystal (Table 2). This shows that the increased dihedral twist, θ , leads to the strong decrease in the hyperpolarizability of BHPDQ in the crystalline state, overwhelming the influence of the quinonoid–benzenoid factor.

Powder SHG measurements carried out on BHPDQ indicated that the SHG intensity saturated at 13 U for particle sizes of $\geq 250 \mu\text{m}$; the SHG was found to be 0.09 times that of NPP of similar particle size. Similar SHG was found for crystals as well, indicating that this material is phase-matchable.¹⁷ We can relate the observed SHG to the molecular dipole orientation in

Table 3. The Static β Values from AM1 Computation, Interdipole Vector Angles, α from Crystal Structure Analysis, the Computed Enhancement/Reduction Factor (f), and the Powder SHG Values for Four SHG Active Compounds

compd	$-\beta$ (10^{-30} esu)	α (deg)	f	$f \beta $ (10^{-30} esu)	powder SHG (U)
MBPDQ ^a	51.0	168	0.21	10.7	3
BHPDQ	31.3	126, 114	0.89	27.9	13
PMPDQ ^a	51.4	94, 149	0.99	50.4	28
DMPDQ ^b	50.2	103	1.25	62.8	55

^a Reference 14. ^b Reference 15

BHPDQ, resulting from the combined influence of molecular chirality and H-bond network. The sum of two dipole vectors oriented at an angle (α) can be expressed using the simple relation¹⁵

$$f = \sqrt{2(1 + \cos \alpha)}$$

[The oriented gas model²⁷ also provides this expression if one considers only the major component of the microscopic (β_{iii}) and macroscopic (d_{III}) NLO coefficients, assumes two equivalent molecular sites in the unit cell, and neglects local field factors.] The enhancement/reduction factor, f (strictly $0.5f$), indicates approximately the effective contribution of individual molecular hyperpolarizability to the bulk NLO susceptibility and has been shown to correlate well with the bulk SHG of three compounds analyzed earlier. In the BHPDQ crystal there are four molecules in the unit cell with interdipole vector angles of 114° and 126° . The factor f can be computed by considering any one dipole vector and the addition of the other three vectors to it using

$$f = \prod_i \sqrt{2(1 + \cos \alpha_i)}$$

where $i = 3$. f is found to be 0.89 for BHPDQ. Table 3 provides the values of f calculated for MBPDQ,¹⁴ PMPDQ,¹⁴ and DMPDQ¹⁵ along with the value for BHPDQ (we note that there is a minor error in the value for PMPDQ given in ref 15, since only two of the three angles were considered in the computation of f ; however, the correction in the value is very small and conclusions drawn earlier remain unchanged). The table also presents β values computed for the molecular structures from each of the crystal structures. We find that the powder SHG correlates very well with the factor $f\beta$ for the four-point data set (Table 3 and Figure 5). Though the β of BHPDQ is lowered due to the molecular twist, the dipole alignment is good, leading to the appreciable SHG capability of 13 U. It may be noted that the earlier three compounds had very similar β values and hence the solid-state SHG scaled, almost trivially, with the f factor. This study of BHPDQ has therefore been crucial in revealing the more complex correlation of the material NLO property to the combined quantity $f\beta$.

β and f could be considered as the representations of the molecular and crystal contributions to the solid-state SHG capability. Molecular structure influences the solid state SHG through the hyperpolarizability. The molecular structure together with intermolecular interactions such as H-bonding determines the crystal

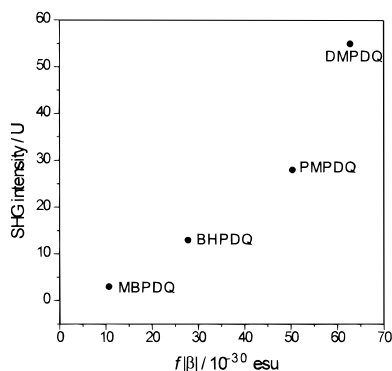


Figure 5. The correlation of the powder SHG with the factor $f\beta$ for four push-pull quinonoid molecular materials.

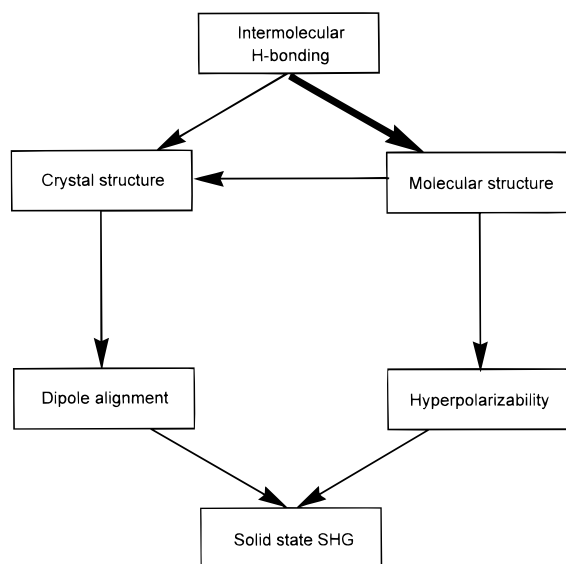


Figure 6. Schematic diagram of various factors which contribute to the solid-state SHG in molecular materials (the thick line indicates the new observation in this study).

structure which has a direct bearing on the solid-state SHG. The effect of intermolecular interactions on the molecular structure is usually quite small; for example, bond lengths are modified slightly when one of the atoms involved in the bond takes part in a H-bond as well. A search of noncentrosymmetric crystal structures in the Cambridge Crystallographic Database revealed that there are some instances²⁸ in which intermolecular H-bonding probably influences the molecular conformations; however, this aspect has not been analyzed in any detail. The present observation is a rare and interesting case of intermolecular interactions exerting a profound influence on the molecular structure and thus on the molecular and material properties. We schematize this paradigm in Figure 6.

We have examined the significance of the chiral nature of BHPDQ, by carrying out the reaction of the racemic mixture of 3-hydroxypyrrolidine with TCNQ. The product is optically inactive, indicating that it is

probably an [(*R,R*)/(*S,S*)] or an (*R,S*) form or mixture of both; chromatographic and NMR spectroscopic studies did not lead to an unequivocal conclusion whether it is a mixture of diastereomers or not. However this material shows a reproducible and stable, though quite weak (~ 1 U), solid-state SHG. The observation of SHG indicates that a noncentric lattice is formed. Either a noncentric arrangement of a pair of enantiomers is formed in the unit cell or a spontaneous resolution of the (*R,R*)/(*S,S*) mixture with each microcrystal being homochiral has occurred. Since we could not obtain good quality crystals, the crystal structure was not determined. However this control experiment shows that the presence of chirality in BHPDQ is crucial for achieving the dipole alignment and the pronounced SHG capability. Further, the product from racemic hydroxypyrrolidine has the usual light yellow color of the push-pull quinonoid materials, in strong contrast to BHPDQ. This indicates that the chirality and the unique H-bonded structure of BHPDQ leading to its enhanced molecular twist gives rise to the improved transparency in this interesting material.

Conclusion

We have synthesized and investigated a new member of the push-pull quinonoid molecular materials which are promising candidates for SHG applications. The new system, BHPDQ is unique in this series in terms of the extensive intermolecular H-bonding present in its crystal lattice. The H-bonds exert a strong influence, in conjunction with the molecular chirality, on the alignment of the dipoles leading to an effective contribution of 45% ($f = 0.89$) of the molecular hyperpolarizability to the bulk susceptibility. More significantly, the intermolecular H-bonds lead to an enhanced twist in the molecule and, as a consequence, a reduced hyperpolarizability. The two factors together lead to an effective powder SHG capability of 13 U in BHPDQ. The positive impact of the molecular structure modification by the H-bond network is the improved transparency of BHPDQ in the solid state. The structure and NLO property of BHPDQ reveals important aspects of the impact of crystal forces on molecular structure. This should provide impetus for careful fine-tuning of the material property, not only through direct manipulation of the crystal structure but also through concomitant modifications of the molecular framework.

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Supporting Information Available: Listing of atomic coordinates, bond distances, and angles, least-squares planes, thermal parameters from X-ray crystal structure analysis for the compound BHPDQ (8 pages); observed and calculated structure factors (11 pages). See any current masthead page for ordering information.

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