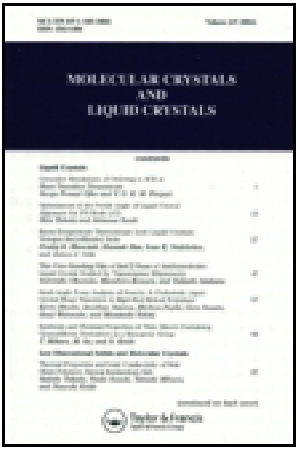

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Control of Crystal Packing in SHG Active 7,7-Bis(n-pentylamino)-8,8-dicyanoquinodimethane by Intermolecular H-bonds and Alkyl Chain Interactions

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Our recent studies have shown that simple alkyl chains can be used as crystal design elements to drive the formation of noncentrosymmetric lattices of interest in quadratic nonlinear optical applications. In a series of alkyl substituted diaminodicyanoquinodimethanes second harmonic generation was observed only in the systems with intermediate chain length. The molecular and crystal structures of 7,7-bis(n-pentylamino)-8,8-dicyanoquinodimethane, one of the SHG active crystals in this series, are presented in this paper. Dipolar, H-bonding and alkyl chain interactions are observed between the molecules in the crystal. Semiempirical quantum chemical computations on the molecule and detailed analysis of the experimental molecular and crystal structures reveal the critical role played by alkyl chain interactions in the formation of the noncentric lattice and the resultant SHG capability of this material.

INTRODUCTION

Organization of molecules in a preordained fashion to achieve desired material properties is the basic paradigm in molecular materials research. Examples include formation of regular, segregated stacks of donor/acceptor molecules with partial ionicity to produce molecular conductors,[1] appropriate orientation of π-radicals to maximize negative spin density products in organic magnets[2] and noncentrosymmetric lattice formation with suitable alignment of hyperpolarizability tensor components in molecular materials for quadratic nonlinear optical (NLO) applications.[3] Molecules having a conjugated π-electron system asymmetrically polarized using appropriate donor/acceptor substituents usually show

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high hyperpolarizabilities, β and are of great current interest in NLO applications such as second harmonic generation (SHG). However the assembly of such molecules into bulk materials such as crystals or thin films with suitable alignment of the β tensor components has been hampered by the dominant tendency of organic molecules to form centrosymmetric lattices. A wide variety of chemical as well as physical approaches have been investigated to circumvent this problem. Molecular modifications investigated include incorporation of effects such as chirality,[4] intermolecular H-bonding,[5] dipole cancellation[6] and steric factors.[7] Physical techniques such as electric field poling of the NLO chromophores embedded in polymer matrices[8] and formation of noncentric X or Z type Langmuir-Blodgett films[9] have also been utilized.

Based on the early work from du Pont on amino derivatives of tetracyanoquinodimethane[10]we have developed a new class of materials for SHG. These push-pull quinonoid molecules possess large hyperpolarizability and effects such as chirality,[11] H-bonding[12] and solvate loss[13] have been used to achieve moderate to strong SHG capability in the corresponding molecular materials. Recently we have discovered that introduction of alkyl chains of appropriate length is a simple molecular modification that could be used to generate noncentrosymmetric crystal lattices of achiral molecules capable of moderate SHG. Our studies on two series of NLO chromophores based on diaminodicyanoquinodimethane[14] and p-nitroaniline[15] having alkyl chain substituents from propyl to octyl showed that short as well as long alkyl chains encourage centrosymmetric lattice formation whereas noncentric lattices are formed when intermediate chain lengths are involved. In the short chain systems the dipolar interactions dominate and in the long chain systems the alkyl chain interactions become assertive. The success of the intermediate chain molecules was attributed to the subtle interplay of dipolar, H-bonding and alkyl chain interactions. The butyl, pentyl and hexyl substituted diaminodicyanoquinodimethanes and the butyl substituted p-nitroaniline showed powder SHG ranging from 10 – 20 U (1 U = SHG of urea).

Besides the SHG capability of these materials, their crystal structures reveal a number of interesting features of value to crystal structure design. The intermolecular interactions that lead to the noncentric structure were briefly outlined in Ref.14 by comparing the structure of SHG active 7,7-bis(n-butylamino)-8,8-dicyanoquinodimethane with that of the SHG inactive propyl and octyl derivatives. We present in this paper a detailed analysis of the molecular structure of 7,7-bis(n-pentylamino)-8,8-dicyanoquinodimethane (BPNDQ) obtained from single crystal x-ray study and in conjunction with semiempirical computations we probe the dependence of its hyperpolarizability on structural parameters. The critical role of intermolecular H-bonding and alkyl chain interactions that leads to the formation of noncentrosymmetric crystal lattice in this material is also examined.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

BPNDQ was synthesized following the general procedure reported earlier.[10,14] 400 mg (1.96 mmol) of tetracyanoquinodimethane was dissolved in 15 ml of freshly dried and distilled acetonitrile and warmed to 60°C. 1.13 ml (9.8 mmol) of n-pentyl amine was added (CAUTION: HCN gas is the byproduct in this reaction). The solution initially turned green and subsequently changed to dark brownish yellow; light yellow colored precipitate formation was also observed. It was stirred for 2.5 hours, cooled to 10°C and filtered. The filter cake was washed with ether and dried to give 419 mg (81% yield) of BPNDQ. It was recrystallized from acetonitrile. Characterization and powder SHG studies of BPNDQ are reported in Ref.14. BPNDQ showed phase matched SHG of 11.9 U.

X-ray diffraction data were collected on an Enraf-Nonius MACH3 diffractometer. MoK_α radiation with a graphite crystal monochromator in the incident beam was used. Data was reduced using Xta13.4;[16] Lorentz and polarization corrections were included. All non-hydrogen atoms were found using the direct method analysis in SHELX-97[17]and after several cycles of refinement the positions of the hydrogen atoms were calculated and added to the refinement process. Graphics were handled using ORTEX6a.[18]Details of data collection, solution and refinement, anisotropic thermal parameters and full lists of bond lengths and angles are deposited with Cambridge Crystallographic Data Center.

AM1 semiempirical calculations[19] were carried out using MOPAC93[20] program imposing the PRECISE option in all calculations. Hyperpolarizabilities were evaluated using the CPHF procedure[21] implemented in MOPAC93. The values reported are the static values, β_0 corresponding to zero excitation energy.

RESULTS AND DISCUSSION

Colorless, transparent crystals of BPNDQ were grown from acetonitrile by slow evaporation of the solvent. Interestingly we find that BPNDQ can be grown into fairly large crystals (~ $9 \times 5 \times 2\ mm^3$). It shows good thermal stability, melting at 244 – 246°C. However the crystals are found to be soft and flaky rendering cutting and polishing difficult. Single crystal analysis showed that BPNDQ belongs to the orthorhombic Fdd2 space group with one molecule in the asymmetric unit. Table I provides the basic crystallographic data. The molecular structure of BPNDQ from x-ray analysis is shown in Fig.1. The fractional atomic coordinates and the significant bond lengths and angles are collected in Table II. Some of the carbon atoms in the alkyl chains show large thermal parameters indicating fair amount of motion and this leads to some unlikely bond lengths in the chain. One of the alkyl chains is oriented *syn* with respect to the six-member ring and the other *anti*; the respective dihedral angles are 16.4° and 179.1°. The chain oriented *syn* has an all-trans conformation whereas the *anti* chain has one bond (C21-C22) in *gauche* conformation. The dicyanomethylene group is essentially coplanar with the six-member ring, but the diaminomethylene unit is twisted out of this plane by an angle $\theta \sim 47°$. This twist is a common feature in these push-pull quinonoid molecules;[11,12] it arises as a result of the steric repulsion between the *ortho* H atoms on the ring and the alkyl amino groups and points to the fact that the C4-C8 bond is nearly single. Examination of the bond lengths in the six-member ring indicates that it is strongly benzenoid. The push-pull substituents give rise to the benzenoid form and a strongly zwitterionic character for the molecule.

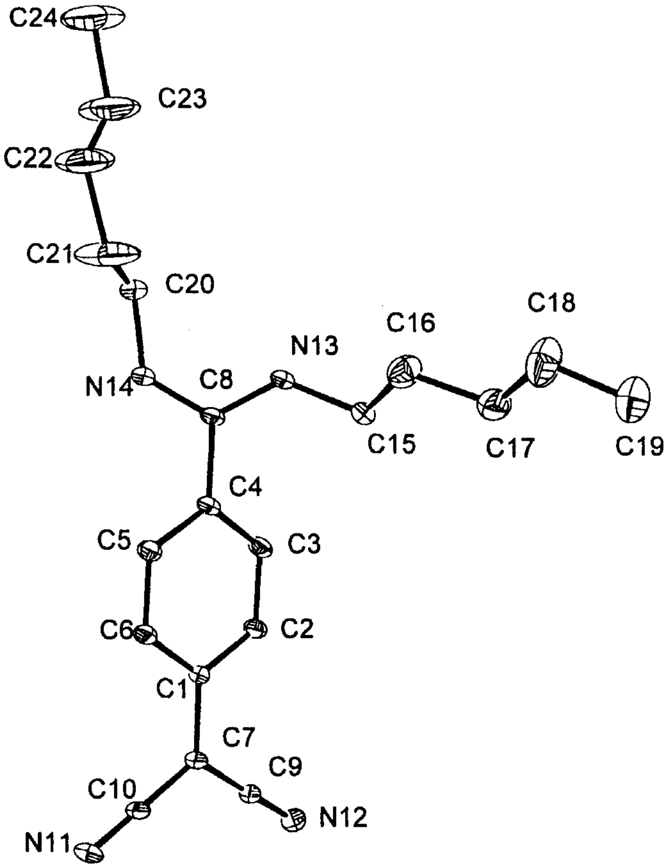

FIGURE 1 Molecular structure of BPNDQ from single crystal x-ray analysis. 10% probability thermal ellipsoids are indicated. H atoms are omitted for clarity

TABLE I Crystallographic data for BPNDQ

Molecular formula	$C_{20}H_{28}N_4$
Formula weight	324.46
Crystal system	Orthorhombic
Space group	Fdd2 (No.43)
a, Å	43.502 (3)
b, Å	20.600 (3)
c, Å	9.2728 (12)
α, deg.	90.0
β, deg.	90.0
γ, deg.	90.0
V, $Å^3$	8309.9 (17)
Z	16
ρ_{calc}., g cm^{-3}	1.037
Temperature	293 K
μ, cm^{-1}	0.63
λ (Å)	0.71073
no. unique reflections	3570
no. of reflections with $I > 2\sigma_I$	2421
no. of parameters	219
R (for $I > 2\sigma_I$)	0.0559
wR^2	0.1604

TABLE II (**a**) Fractional atomic coordinates ($\times$ 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$), (**b**)significant bond lengths and (**c**) significant bond angles and dihedrals in BPNDQ from single crystal x-ray study

(a)

Atom	x	*y*	*z* U_{eq}	
C1	264(1)	2134(1)	1017(3)	59(1)
C2	122(1)	2497(1)	−72(3)	73(1)
C3	182(1)	3143(2)	−247(3)	76(1)
C4	382(1)	3470(1)	675(3)	64(1)
C5	517(1)	3116(1)	1784(3)	67(1)
C6	461(1)	2467(1)	1944(3)	65(1)
C7	203(1)	1443(1)	1160(3)	66(1)
C8	434(1)	4176(1)	517(3)	68(1)
C9	7(1)	1137(1)	191(3)	80(1)
C10	339(1)	1068(1)	2243(4)	73(1)
N11	442(1)	763(1)	3145(4)	100(1)
N12	−159(1)	898(2)	−614(4)	105(1)
N13	492(1)	4435(1)	−739(3)	80(1)
N14	411(1)	4535(1)	1664(3)	95(1)

(a)

Atom	×	*y*	*z* U_{eq}	
C15	589(1)	4104(2)	−2065(4)	98(1)
C16	870(1)	4359(3)	−2694(7)	129(2)
C17	963(2)	4040(3)	−4118(8)	132(2)
C18	1224(2)	4290(5)	−4824(10)	200(4)
C19	1303(2)	3942(5)	−6190(8)	175(3)
C20	449(2)	5242(2)	1741(5)	121(2)
C21	707(2)	5462(3)	2192(16)	273(9)
C22	750(3)	6190(5)	2460(2)	295(8)
C23	732(6)	6590(5)	2000(3)	452(17)
C24	805(4)	7299(4)	2180(2)	327(11)

(b)

Bond	*Length (Å)*
N14 – C8	1.300(4)
N14 – C20	1.468(4)
N13 – C8	1.306(4)
N13 – C15	1.469(5)
N12 – C9	1.150(5)
N11 – C10	1.139(5)
C1 – C6	1.393(4)
C1 – C2	1.401(4)
C1 – C7	1.454(3)
C2 – C3	1.367(4)
C3 – C4	1.392(4)
C4 – C5	1.390(4)
C4 – C8	1.479(4)
C5 – C6	1.368(4)
C7 – C9	1.388(5)
C7 – C10	1.398(5)

(c)

Bond – bond / – bond	*Angle (°)*
C8 – N14 – C20	126.6(3)
C8 – N13 – C15	127.7(3)
C6 – C1 – C2	116.9(2)
C6 – C1 – C7	122 6(2)
C2 – C1 – C7	120.4(3)
C3 – C2 – C1	121.3(3)

(c)

Bond – bond / – bond	*Angle (°)*
C2 – C3 – C4	121.2(2)
C5 – C4 – C3	117.8(2)
C5 – C4 – C8	121.5(3)
C3 – C4 – C8	120.6(2)
C6 – C5 – C4	121.0(3)
C5 – C6 – C1	121.7(2)
C9 – C7 – C10	118.2(2)
C9 – C7 – C1	119.8(3)
C10 – C7 – C1	122.0(3)
N14 – C8 – N13	120.7(2)
N14 – C8 – C4	117.9(3)
N13 – C8 – C4	121.4(3)
N12 – C9 – C7	178.3(4)
N11 – C10 – C7	178.2(4)
C2 – C1 – C7 – C9	1.6(4)
C6 – C1 – C7 – C10	−0.2(4)
C20 – N14 – C8 – C4	−179.1(4)
C15 – N13 – C8 – C4	−16.4(6)
C5 – C4 – C8 – N14	−46.5(5)
C3 – C4 – C8 – N13	−47.6(5)

Our earlier semiempirical computational studies[22] have shown that the quinonoid-benzenoid character of the six-member ring strongly influences the hyperpolarizability. A parameter QBC was defined based on the bond lengths in the ring such that the quinone structure has a value of 0 and the benzene structure a value of 1.0. It was found that the β calculated in the absence of an applied field increases almost linearly with QBC. The β is also sensitive to the twist angle θ showing a maximum near 60°.[11] To analyze the present case and to gain insight into the role of the conformational structure of the molecule, we have carried out semiempirical AM1 computations starting with the molecular structure determined from the single crystal study. In addition to the experimental molecular structure we have considered for geometry optimization, three cases in terms of the conformational orientation of the alkyl chains: (i) *syn* and *anti* as in the experimental geometry, (ii) both *syn* and (iii) both *anti*. In each case we have carried out full geometry optimization as well as partial optimization keeping the diaminodicyanoquinodimethane moiety fixed at the experimental geometry and allowing only the alkyl chains to optimize. We noticed that changing the chain with one *gauche* conformation into an all-trans form led to only negligible changes in all the computed values; we therefore report the results based on the all-trans conformation. The computed values of the heats of formation, twist angle, dipole moment and β_0 are presented in Table III.

TABLE III AM1 computed heats of formation ΔH_f, twist angle θ (the two possible dihedral angles are very close and hence averaged), dipole moment μ and static hyperpolarizability β_0 for the experimental and different partially and fully optimized structures of BPNDQ

Conformer	*Optimization*	ΔH_f / *kcal mol*$^{-1}$	θ /°	μ / *D*	β_0 / *esu*
anti / syn	None[a]	958.5	47.1[b]	21.5	102 2
anti / syn	alkyl chains alone	173.7	47.1	21.4	94.2
anti / syn	full structure	68.2	35.7	17.1	43.1
anti / anti	alkyl chains alone	174.8	47.1[b]	22.6	103.7
anti / anti	full structure	67.6	34.7	16.6	43.5
syn / syn	alkyl chains alone	177.9	47.1[b]	20.4	83.4
syn / syn	full structure	73.8	31.0	14.5	16.7

a. Single point calculation on the experimental geometry
b. Experimental value

The unnaturally high heat of formation computed for the experimental geometry is a consequence of the unrealistic bond lengths in the alkyl chains as seen from the drastic reduction in the heat of formation once the chains are optimized. Since the basic π-electronic structure is not changed at this stage the β_0 values are affected very little. Full optimization of the molecular geometry lowers the heat of formation further, but more significantly it leads to a lower dipole moment as well as β_0. The latter results from a combination of two related effects - the transformation of the six-member ring from a benzenoid to a quinonoid form and the decrease in the twist angle. The former can be quantified by the change in QBC value from 0.733 to 0.370. The zwitterionic benzenoid structure is stabilized in the highly polar environment in the crystal lattice and the more quinonoid form appears to be the stable gas phase structure mimicked by the computation. The decrease in θ on optimization indicates that the crystal packing forces support an increased molecular twist contributing to the enhancement of β_0. The partially optimized *anti/anti* conformer shows a higher β_0 than that of the corresponding *anti/syn* form, however its heat of formation suggests that it is likely to be less stable. The optimized *anti/anti* and *syn/syn* conformers showed similar or slightly higher heats of formation suggesting that the *anti/syn* conformer is indeed one of the preferred geometries. The *anti/anti* structure shows twist angles, dipole moments and β_0 values comparable to that of the *anti/syn* structure. The *syn/syn* structure however has a lower twist angle and dipole moment and reduced β_0. From these computations we conclude that the

BPNDQ molecule is stabilized in a zwitterionic benzenoid form in the crystal lattice and the chain conformations and molecular twist are conducive to the enhancement of the molecular hyperpolarizability.

The zwitterionic form points to the presence of strong dipolar forces operative in the crystal. Generally the electrostatic interactions encourage an antiparallel alignment of the dipolar molecules often leading to centrosymmetric packing motifs. In BPNDQ these dipolar interactions lead to a nearly antiparallel alignment of the major dipole axes of neighboring molecules; the vector connecting the diaminomethylene carbon to the dicyanomethylene carbon atom defines the major dipole axis and such vectors of near neighbor molecules are at an angle of 168.1°. However the benzenoid rings of these molecules are tilted with respect to each other with the angle between their mean planes being 74.8° (Fig.2). This leads to the breaking of the center of inversion in much the same way as it happens in the prototypical urea crystal.[23] The noncentric packing in BPNDQ owes its origin to the presence of some subtle interactions besides the strong dipolar forces and we examine these factors below.

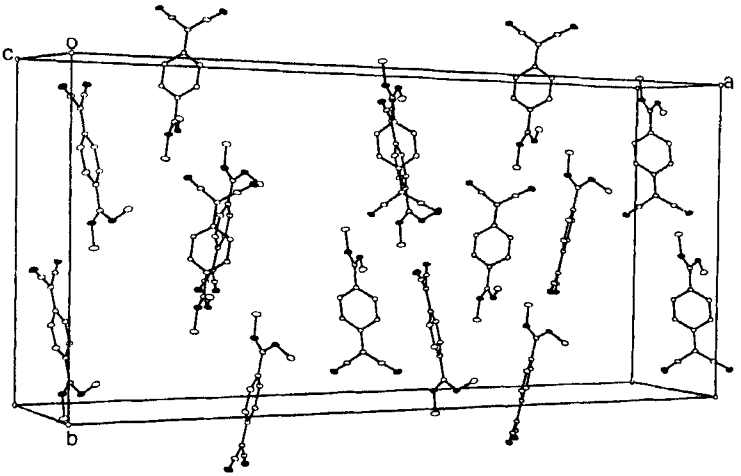

FIGURE 2 Unit cell of BPNDQ showing the tilted orientation of near neighbor molecules. All hydrogen atoms and carbon atoms beyond the first one in each alkyl chain are omitted for clarity. Nitrogen atoms are shown as filled circles

The crystal structure of BPNDQ reveals a number of interesting features. Strong H-bonds are observed connecting (A) N11 and N13 atoms (2.930 Å) and (B) N12 and N14 atoms (2.893 Å) of near neighbor molecules (Fig.3). The A type H-bonds link molecules into extended chains with opposite polarity running

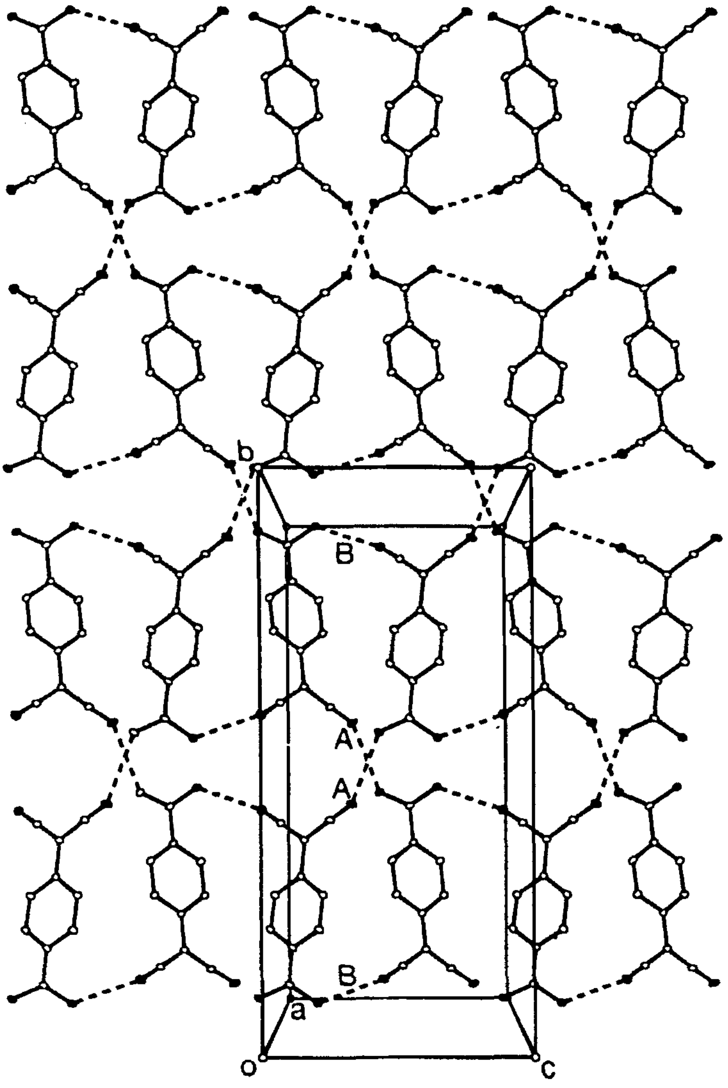

FIGURE 3 H-bond network in BPNDQ. View along the *a* axis is shown. All hydrogen atoms and carbon atoms of the alkyl chains are omitted for clarity. Nitrogen atoms are shown as filled circles and the H-bonds are indicated by the broken lines. See text for the meaning of the designations A and B

approximately along the [011] and $[01\bar{1}]$ directions and the B type serve as cross links between them. The result is a beautiful two-dimensional network extending in the *bc* plane. Search for short contacts between carbon atoms of the alkyl chains of neighboring molecules revealed several of them in the range 3.8 – 4.1 Å (Fig.4). C20 atoms in the *anti* chains of oppositely oriented neighboring molecules have a contact distance of 4.048 Å (A in Fig.4). The terminal carbon (C24) of these chains have two close contacts B and C of 3.856 Å and 3.904 Å respectively with C17 and C15 of the *syn* chain of a neighbor. The terminal carbon (C19) of the *syn* chains of another neighbor has a close contact D of 4.085 Å with C22 of the *anti* chain. The nonbonded carbon atom interactions A, B and C form a close-knit network around oppositely aligned BPNDQ molecules which form part of the H-bonded network discussed above. The D contacts are found between adjacent H-bonded two-dimensional sheets. The most significant impact of the combination of the various H-bond and alkyl chain interactions described above appears to be the tilting of the ring planes of the oppositely aligned BPNDQ molecules.

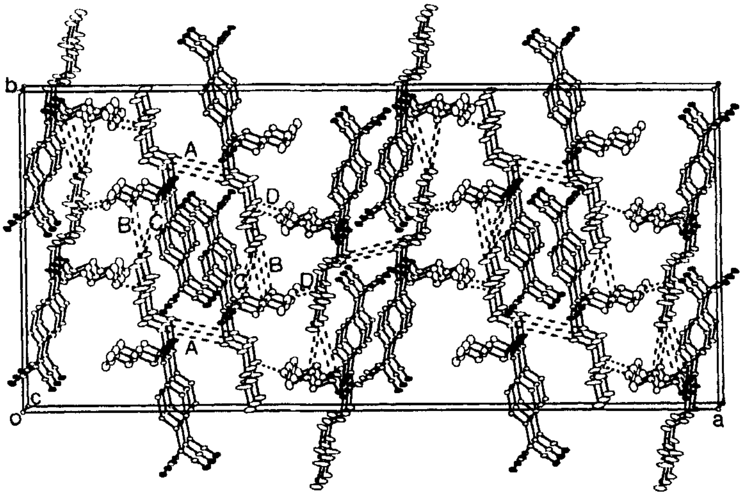

FIGURE 4 Alkyl chain interactions in BPNDQ. View along the *c* axis is shown. Hydrogen atoms are omitted for clarity. Nitrogen atoms are shown as filled circles and the short intermolecular carbon atom contacts are indicated by the broken lines. See text for the meaning of the designations A, B, C and D

The dipolar interactions, intermolecular H-bonds and alkyl chain interactions together lead to a noncentric crystal structure in BPNDQ. The dipolar interactions and the potential for H-bonds are similar in the whole series of alkylamino substituted dicyanoquinodimethanes. However a noncentric lattice and SHG activity is observed only in BPNDQ and the butyl and hexyl derivatives. This shows that alkyl chains of intermediate length are important and the interactions of such chains play the critical role in developing the noncentric lattice in these systems. The hyperpolarizability of these push-pull quinonoid molecules are generally large and as seen from the computations above, the alkyl chain dispositions and molecular twist enhance the β of BPNDQ molecule in the crystal. Therefore even though the major β tensor component is nearly canceled, the other components ensure a moderate SHG in this material.

CONCLUSION

The utility of alkyl chains as novel design elements for noncentrosymmetric crystal lattices has prompted a detailed analysis of the crystal packing in bis(alkylamino)dicyanoquinodimethanes. We have presented in this paper, the molecular and crystal structure of BPNDQ, the pentyl derivative. The molecular structure is examined in the light of semiempirical quantum chemical computations. The impact of the polar environment in the crystal on the molecular structure and hyperpolarizability are revealed. The role of the disposition of the alkyl chains and the molecular twist in enhancing the molecular hyperpolarizability are examined. Detailed analysis of the crystal structure of BPNDQ shows that even though dipolar interactions are likely to be the dominant crystal packing forces, subtle effects of intermolecular H-bonding and alkyl chain interactions play the crucial role of symmetry breaking in this material.

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