

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230724683>

Chiral Vicinal Bis(amide) Molecules: Polar/Helical Assemblies in Crystals and Second Harmonic Generation

ARTICLE *in* CRYSTAL GROWTH & DESIGN · JUNE 2005

Impact Factor: 4.89 · DOI: 10.1021/cg0501231

CITATIONS

20

READS

39

3 AUTHORS, INCLUDING:



Savarimuthu Philip Anthony

SASTRA University

64 PUBLICATIONS 561 CITATIONS

SEE PROFILE

Communications

Chiral Vicinal Bis(amide) Molecules: Polar/Helical Assemblies in Crystals and Second Harmonic Generation

S. Philip Anthony, K. Basavaiah, and T. P. Radhakrishnan*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Received April 3, 2005

ABSTRACT: A family of organic and metal–organic materials based on chiral vicinal bis(amide) structures are developed. Subtle molecular structure variations give rise to polar and helical organizations in crystals of the two basic compounds *N,N'*-bis(benzoyl)-(1*R*,2*R*)-diaminocyclohexane and *N,N'*-bis(isonicotinoyl)-(1*R*,2*R*)-diaminocyclohexane; they exhibit the unusual syn and normal anti conformations of the bis(amide) group, respectively. The new materials exhibit appreciable thermal stability and optical transparency. Trends in their second harmonic generation capability are analyzed.

Molecular assembly in crystals is controlled by the molecular structure and intermolecular interactions. For example, homochirality of the molecular building blocks ensures noncentrosymmetry in the bulk material, and conformational flexibility can have a profound influence on the molecular organization in the solid state.¹ Networking of molecules through interactions such as H bonds and metal coordination can be exploited to generate a range of fascinating solid-state structures.^{2,3} Focus of the majority of molecular materials research has been on fabricating molecular assemblies fine-tuned for enhanced attributes such as electrical, magnetic, and optical or nonlinear optical (NLO) characteristics. In the case of NLO materials, the primary goal has been to achieve strong nonlinear responses such as second harmonic generation (SHG). Several approaches have been developed to obtain noncentrosymmetric structures with optimal molecular orientations; however, special motifs such as polar and helical structures remain important targets because of their potential utility in specific nonlinear optical and optoelectronic applications.^{4,5} Even though molecular NLO materials possess advantages such as high nonlinear susceptibilities, low refractive indices, and tailorability of molecular and solid-state organization, their application potential is limited by poor mechanical and thermal stabilities as well as low transparency at wavelengths of interest. Taking these aspects into consideration, we have been investigating novel ligand designs for generating coordination polymers capable of optical SHG.^{6,7}

Chiral bis(amide) molecules would be interesting candidates, since they combine features required for noncentrosymmetric organization (chirality) and extended intermolecular interactions (complementary H-bond functionalities). We present here the molecular and crystal structures of two basic molecules, *N,N'*-bis(benzoyl)-(1*R*,2*R*)-

diaminocyclohexane (BBDC) and *N,N'*-bis(isonicotinoyl)-(1*R*,2*R*)-diaminocyclohexane (BINDC), in a new family that we have investigated. Helical organization mediated by H bond interactions are observed in crystals of *C*₂-symmetric BINDC. Interestingly, the closely related BBDC is found to possess a very different structure exhibiting polar organization which stems from a syn conformation of the vicinal bis(amide) group: i.e., a conformation in which the two amide dipoles point in similar directions. To the best of our knowledge a syn conformation is unprecedented in such free vicinal bis(amide) structures; it has been obtained only due to constraints such as metal coordination⁸ or cyclic structure formation.⁹ We have synthesized several derivatives of BBDC and coordination polymers of Ag(I) and Zn(II) with BINDC. In this communication, we briefly note the high thermal stability and broad optical transparency of these materials and the trends in their SHG capability.

BBDC was synthesized¹⁰ by the reaction of (1*R*,2*R*)-diaminocyclohexane with benzoyl chloride in the presence of sodium hydroxide;¹¹ the stereochemistry of this compound in solution¹² and the use of a phosphino derivative in enantioselective reactions¹³ have been investigated earlier. Crystals of BBDC grown by slow evaporation of a methanol solution are found to belong to the *P*2₁ space group with one molecule in the asymmetric unit (Table 1). The molecule possesses an unusual syn conformation of the bis(amide) group (Figure 1a). The short intermolecular N–H···O bonds (*r*_{N4···O1} = 2.793 Å, *θ*_{N4–H4···O1} = 153.6°; *r*_{N8···O2} = 2.959 Å, *θ*_{N8–H8···O2} = 164.1°) lead to extended polar chains along the *b* direction (Figure 2). Screw rotation (about *b*) being the only symmetry element present, all the chains in the crystal are oriented in the same direction. BINDC was synthesized by the reaction of (1*R*,2*R*)-diaminocyclohexane with isonicotinoyl chloride in the presence of triethylamine.¹¹ Crystals grown by slow evaporation of a methanol solution belong to the *P*2₁2₁2₁ space group with one molecule in the asymmetric unit (Table 1, Figure 1b). The bis(amide) group in BINDC is disposed in the normal

* To whom correspondence should be addressed. Tel: 91-40-2301-1068. Fax: 91-40-2301-2460. E-mail: tprsc@uohyd.ernet.in. Web: http://202.41.85.161/~tpr/.
~tpr/.

Table 1. Crystallographic Data for BBDC and BINDC

	BBDC	BINDC
empirical formula	C ₂₀ H ₂₂ N ₂ O ₂	C ₁₈ H ₂₀ N ₄ O ₂
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	9.2636(9)	5.1328(4)
<i>b</i> /Å	9.7900(9)	17.2924(14)
<i>c</i> /Å	10.7319(10)	18.9976(15)
β /deg	115.0250(10)	90
<i>V</i> /Å ³	881.91(14)	1686.2(2)
<i>Z</i>	2	4
ρ_{calcd} /g cm ⁻³	1.214	1.278
μ /mm ⁻¹	0.079	0.086
temp/K	293(2)	293(2)
λ /Å	0.710 73	0.710 73
no. of rflns measd	10 344	10 863
no. of unique rflns	4044	3904
no. of params	217	217
GOF	0.928	0.880
R1 (for $I \geq 2\sigma_I$)	0.0407	0.0440
wR2 (for $I \geq 2\sigma_I$)	0.0801	0.0788
largest diff peak and hole/e Å ⁻³	0.165, -0.205	0.104, -0.170

anti conformation. As in BBDC, the amide groups enter into strong H bond interactions ($r_{\text{N4}\cdots\text{O2}} = 2.972$ Å, $\theta_{\text{N4-H4}\cdots\text{O2}} = 160.2^\circ$; $r_{\text{N3}\cdots\text{O1}} = 3.033$ Å, $\theta_{\text{N3-H3}\cdots\text{O1}} = 162.4^\circ$) (Figure 4). In addition, there are relatively short intermolecular contacts involving the pyridine nitrogen atom and one of the hydrogen atoms ortho to it ($r_{\text{C22}\cdots\text{N6}} = 3.453$ Å, $\theta_{\text{C22-H22}\cdots\text{N6}} = 149.8^\circ$). These interactions lead to a helical motif extending along the *a* direction (Figure 3). We have synthesized and structurally characterized derivatives of BBDC, *N,N'*-bis(4-*X*-benzoyl)-(1*R*,2*R*)-diaminocyclohexane, where *X* = fluoro (BFBDC), nitro (BNBDC), methoxy (BMBDC), amino (BABDC). They all possess an anti conformation in the solid state; there is no polar assembly, but extended H bonding and helical structures are observed in these materials. We have also investigated novel coordination polymers based on BINDC, with ZnCl₂, ZnBr₂, and Ag(NO₃); they exhibit two-dimensional network structures. The molecular assemblies in these crystals are presented in the Supporting Information and will be the subject of a full paper in the future.

The syn conformation of BBDC in the solid state is unique. Semiempirical AM1¹⁴ and ab initio computations¹⁵

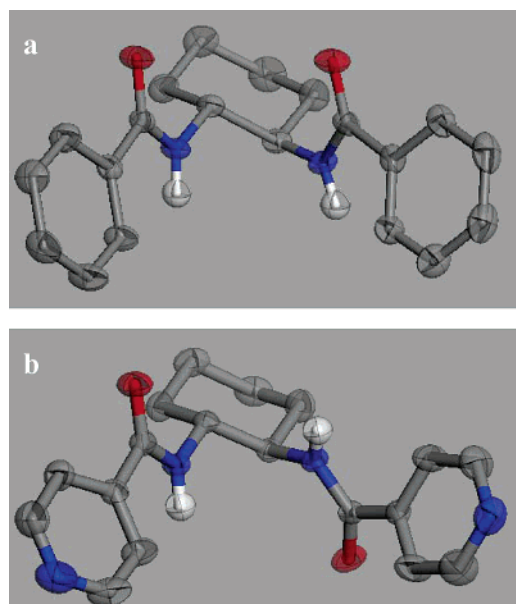


Figure 1. Molecular structure of (a) BBDC and (b) BINDC from crystal structure analysis. Legend: C, grey; N, blue; O, red; H, white. The only H atoms that are shown are those of amino groups, for clarity; 90% probability thermal ellipsoids are indicated.

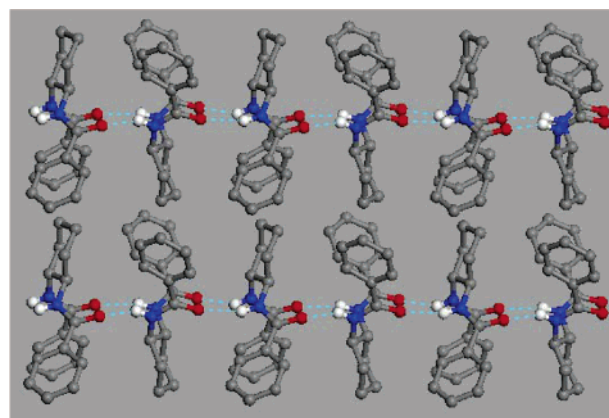


Figure 2. Polar assembly of molecules in crystals of BBDC. Legend: C, grey; N, blue; O, red; H, white; H bonds, broken cyan lines. The only H atoms that are shown are those of amino groups, for clarity.

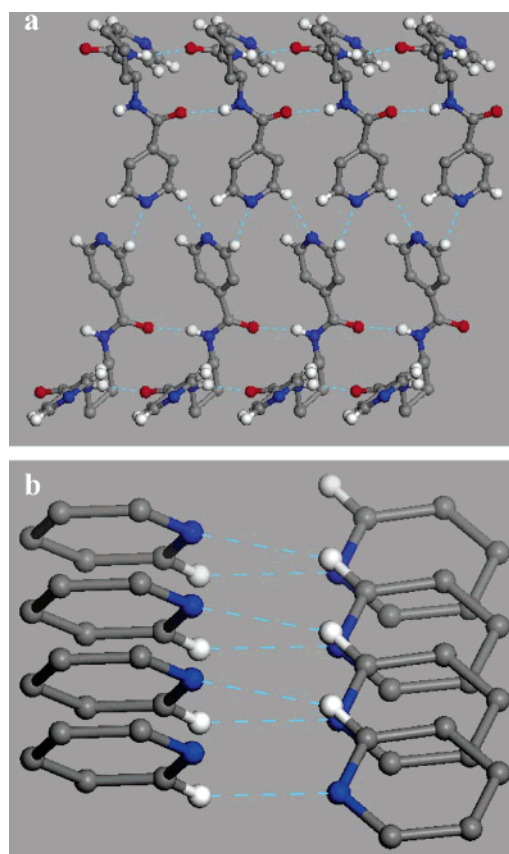


Figure 3. (a) N-H \cdots O and C-H \cdots N intermolecular interactions in crystals of BINDC and (b) the helical motif arising from the latter interactions (the relevant pyridine ring and H atom alone are shown). Legend: C, grey; N, blue; O, red; H, white; H-bond contacts, broken cyan lines. Most of the H atoms are omitted for clarity.

at the B3LYP/6-31G* level showed that the anti conformer is more stable by 6–8 kcal/mol; the case with BINDC is similar.¹¹ The CD spectra of BBDC and its derivatives (Figure 4) are consistent with the earlier report on BBDC¹² and suggest a similar conformation and helicity in solution. On the basis of the solid-state structures of the derivatives, computational results, and CD spectra, we infer that BBDC and its derivatives possess an anti conformation in solution. This implies that the syn conformer in the crystals of BBDC results from solid-state effects alone; this is significant,

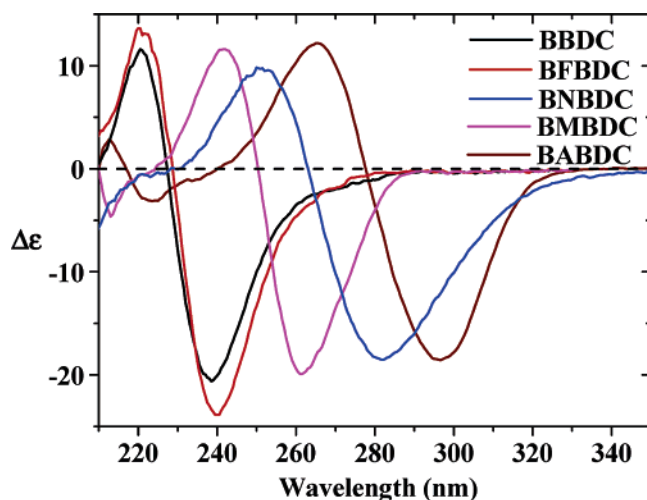


Figure 4. CD spectra of BBDC and its derivatives in methanol solution.

Table 2. Melting Temperatures from Differential Scanning Calorimetry and Electronic Absorption Data for BBDC and Its Derivatives and BINDC and Its Coordination Polymers^a

compd	melting temp (°C)		abs wavelength (nm)	
	onset	peak	λ_{max}	$\lambda_{\text{cut-off}}$
BBDC	257.5	265.6	224.8	287.0
BFBDC	265.0	270.0	225.6	279.4
BNBDc	338.2	340.0	263.6	352.0
BMBDC	264.7	269.0	251.2	289.8
BABDC	285.5	290.0	295.5	327.5
BINDC	267.8	270.0	248.8	304.6
Zn(BINDC)Cl ₂	369.3	373.4	262.0	302.0
Zn(BINDC)Br ₂	406.0	411.3	260.6	306.8
Ag(BINDC)NO ₃	307.3	310.4	258.0	379.8

^a Electronic spectra of the coordination polymers were obtained in aqueous solution and those for the other compounds in methanol solution.

since the syn conformation has made the polar assembly through amide H bonds possible. Introduction of other intermolecular contacts through the ring nitrogen in BINDC or the substituent groups in the BBDC derivatives changes the molecular assembly pattern completely, with the conformation reverting back to anti.

The extended intermolecular interactions in BBDC and BINDC as well as their derivatives and coordination polymers make these materials thermally robust. The melting temperatures of these compounds are collected in Table 2. The wavelengths corresponding to the electronic absorption peak and cut-off are also shown in the table. The data clearly demonstrate that this new family of materials possesses appreciable thermal stability and optical transparency in the full visible range.

The molecular structures of the chiral bis(amide) molecules do not possess any special features that enhance hyperpolarizabilities; however, they serve to monitor fundamental structure–property relations. The β values of the molecular systems were estimated from AM1/TDHF¹⁶ computations (Table 3). Even though BBDC and BINDC and their derivatives with electron-withdrawing groups possess small values, the methoxy- and amino-substituted BBDC show higher hyperpolarizabilities. Kurtz–Perry powder measurements¹⁷ were carried out to evaluate the bulk SHG response (at 532 nm) of the new materials. The data are collected in Table 3; particle size dependence indicated that all materials are phase matchable.¹¹ Even though BBDC shows no measurable response, BINDC

Table 3. AM1/TDHF Computed Hyperpolarizabilities, β (at Excitation Energy of 1.17 eV), and Solid-State SHG (at 532 nm) of BBDC and Its Derivatives and BINDC and Its Coordination Polymers^a

compd	$\beta_{1,17}/10^{-30}$ esu	SHG/U
BBDC	1.22	0.0
BFBDC	2.11	0.0
BNBDc	2.83	0.0
BMBDC	6.37	0.90
BABDC	11.29	1.82
BINDC	1.24	0.80
Zn(BINDC)Cl ₂		0.38
Zn(BINDC)Br ₂		0.37
Ag(BINDC)NO ₃	—	0.37

^a 1 U = SHG of urea.

shows a moderate value; the helical superstructure possibly promotes the bulk nonlinear response, as observed in earlier cases.⁵ While the derivatives of BBDC with electron-withdrawing groups produce no SHG, the methoxy- and amino-substituted derivatives show a clear response. Since the general crystal packing motifs are similar in these derivatives, the nonlinear response of the bulk materials reflects the trends in molecular nonlinearity. SHG is observed in all the coordination polymers of BINDC but is weak; the reduction from that of BINDC results from the electron-withdrawing effect of the coordinated metal. The observed impacts of the electron-rich groups connected to the amide functionality in improving the solid-state SHG and that of the electron-withdrawing groups or metal complexation in reducing it are consistent with the classical push–pull concepts.⁴

The present work illustrates the generation of polar and helical assemblies in crystals, triggered by subtle variations in simple molecular structures. These molecules serve as the basic frameworks to develop thermally robust, optically transparent organic and metal–organic NLO materials. Simple structure–property correlations are revealed which should enable suitable molecular structure modifications that lead to enhanced second harmonic generation capability in similar materials.

Acknowledgment. Financial support from the DST and CSIR, New Delhi, India, use of the National Single Crystal Diffractometer Facility (DST) at the School of Chemistry, and infrastructure support from the UPE program of the UGC, New Delhi, India, are acknowledged. S.P.A. thanks the CSIR, New Delhi, India, for a senior research fellowship.

Supporting Information Available: Text, tables, and figures giving details of synthesis and characterization, crystal structures, computational procedures and results, and second harmonic generation measurements; crystal data are also given as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Bernstein, J. *Polymorphism in Molecular Crystals*; Oxford University Press: Oxford, U.K., 2002; p 151. (b) Burchell, T. J.; Eisler, D. J.; Puddephatt, R. J. *Chem. Commun.* **2004**, 944.
- (2) (a) Atwood, J. L.; Davies, J. E. D.; Lehn, J.-M.; MacNicol, D. D.; Vogtle, F., Eds. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, U.K., 1996. (b) Schneider, H.-J.; Yatsimirsky, A. K. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
- (3) (a) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, 97, 2005. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, 101, 1629.

- (4) (a) Chemla, D. S.; Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1989; Vols. 1 and 2. (b) Nie, W. *Adv. Mater.* **1993**, *5*, 520. (c) Zyss, J.; Nicoud, J. F. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 533.
- (5) (a) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913. (b) Hoss, R.; König, O.; Kramer-Hoss, V.; Berger, U.; Rogin, P.; Hulliger, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1664. (c) Gangopadhyay, P.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2451. (d) Anthony, S. P.; Radhakrishnan, T. P. *Chem. Commun.* **2001**, 931.
- (6) Anthony, S. P.; Radhakrishnan, T. P. *Chem. Commun.* **2004**, 1058.
- (7) Anthony, S. P.; Radhakrishnan, T. P. *Cryst. Growth Des.* **2004**, *4*, 1223.
- (8) (a) Yamamura, T.; Kuroda, R.; Tadokoro, M. *Chem. Lett.* **1989**, 1807. (b) Cornman, C. R.; Zorinka, E. P.; Boyajian, Y. D.; Olmstead, M. M.; Noll, B. C. *Inorg. Chim. Acta* **1999**, *285*, 134.
- (9) (a) Moberg, C.; Warnmark, K.; Csoregh, I.; Ertan, A. *J. Org. Chem.* **1991**, *56*, 3339. (b) Szumna, A.; Jurczak, J. *Eur. J. Org. Chem.* **2001**, 4031.
- (10) The procedure used is similar to that reported in: Whitener, G. D.; Hagadorn, J. R.; Arnold, J. J. *Chem. Soc., Dalton Trans.* **1999**, 1249.
- (11) See the Supporting Information for details.
- (12) Gawronski, J.; Kolbon, H.; Kwit, M. *Enantiomer* **2002**, *7*, 85.
- (13) (a) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104. (b) Trost, B. M.; Lee, C. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; Chapter 8E.
- (14) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) MOPAC93; Fujitsu Inc., Japan. The molecular structure from the crystal structure and the alternate conformer obtained by rotating one of the amide groups were used as initial geometries for the full optimization calculations.
- (15) *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003. The AM1 optimized structures were used as the initial geometry for the full optimization calculations.
- (16) Dupuis, M.; Karna, S. *J. Comput. Chem.* **1991**, *12*, 487. The AM1 optimized geometries were used in the calculations.
- (17) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

CG0501231