Noncentrosymmetric Organic Solids with Very Strong Harmonic Generation Response

Hong Zhao,[a] Yong-Hua Li,[a] Xi-Sen Wang,[a] Zhi-Rong Qu,[a] Li-Zhong Wang,[a] Ren-Gen Xiong,*[a] Brendan F. Abrahams,[b] and Ziling Xue[c]

Abstract: The molten reaction of 2-naphthol, 4-(aminomethyl)pyridine, and 4-pyridinecarboxaldehyde at about 180 °C yields *trans*-2,3-dihydro-2,3-di(4′-pyridyl)benzo[*e*]indole (**1**) which possesses two chiral centers, rather than an expected Betti-type reaction product with only one chiral carbon center. The same reactions, using 3-pyridinecarboxaldehyde, 4-cyanobenzaldehyde, or 3- cyanobenzaldehyde instead of 4-pyridinecarboxaldehyde produce the related compounds *trans*-2,3-dihydro-2-(4′-pyridyl)-3-(3″-pyridyl)benzo-[*e*]indole (**2**), *trans*-2,3-dihydro-2-(4′-pyridyl)-3-(4″-cyanophenyl)benzo[*e*]indole (**3**), and *trans*-2,3-dihydro-2-(4′-pyridyl)-3-(3″-cyanophenyl)benzo[*e*]indole (**4**), respectively. This reaction proceeds with a high degree of stereoselectivity with a *trans*/*cis* ratio of about 98:2 at elevated temperature. Compounds **1**, **2**, and **4** crystallize in a noncentrosymmetric space group ($Pca2_1$, $Pca2_1$, and Cc), while compound **3** has a chiral space group ($P2_1$). These successfully acentric packing arrangements are probably due to the molecule bearing both two chiral centers and potential hydrogen-bonding groups. Furthermore, the reaction of racemic 6-hydroxy-2′-methyl-2-naphthaleneacetic acid with ethyl-2-cyano-1-(4′-pyridyl)acrylic acetate in the presence of piperidine gives 1-pyridyl-2-ethoxycarbonyl-3-amino-1H-naphtho-[2,1-*b*]pyran-2′-methylacetic acid (**5**), which likewise crystallizes in a chiral space group. All of compounds are second harmonic generation (SHG) active, and have a very strong SHG response approximately about 8.0, 5.0, 12.0, 6.0, and 1.4 (for **1**–**5** compounds) times that of urea. Ferroelectric property measurements indicate that compounds **1**, **2**, **4**, and **5** may display ferroelectric behavior.

Keywords: crystal engineering · ferroelectric behavior · hydrogen bonds · molten reaction · nonlinear optical property

Introduction

Supramolecular chemists have for some time been interested in crystal engineering strategies in attempts to exert control over packing arrangements in organic crystals. It is anticipated that such approaches will lead to the generation of materials that possess technologically useful properties.[1] Of particular importance are nonlinear optical (NLO) function (especially second harmonic generation) and ferroelectric properties because of their practical importance in areas such as telecommunications, optical storage, and information processing.[2] These properties are only found in noncentrosymmetric bulk materials or polar crystals.[3] Although control over the packing arrangements of molecules through the employment of rational design principles has met with some success both for organic and metal–organic coordination polymers,[1,4] crystal engineering has not developed to the stage where a desired structure or crystal symmetry can be ensured.

Despite the fact that racemic mixtures of chiral compounds often give rise to crystallization of centrosymmetric structures,[5] we have discovered a class of compounds, whose members tend to crystallize in acentric space groups. This class contains asymmetric conjugated molecules that offer the prospect of interesting physical properties of the type mentioned above. Herein we report the synthesis and physical properties of this interesting class of compounds.

---

[a] H. Zhao, Y.-H. Li, X.-S. Wang, Z.-R. Qu, L.-Z. Wang,
Prof. Dr. R.-G. Xiong
Coordination Chemistry Institute, The State Key
Laboratory of Coordination Chemistry
Nanjing University, 210093 Nanjing (P. R. China)
Fax: (+86) 25-8331-7761 or (+86)-25–83314502
E-mail: xiongrg@netra.nju.edu.cn

[b] Dr. B. F. Abrahams
School of Chemistry, University of Melbourne
Victoria 3010 (Australia)
Fax: (+61) 3-9347-5180
E-mail: bfa@unimelb.edu.au

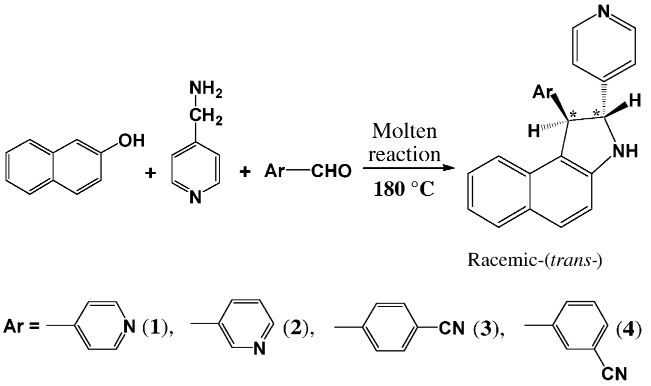
[c] Prof. Dr. Z. Xue
Department of Chemistry, University of Tennessee
Knoxville, TN 37996 (USA)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200305425

Results and Discussion

The molten reaction of 2-naphthol, 4-(aminomethyl)pyridine, and 4-pyridinecarboxaldehyde at about 180 °C produces *trans*-2,3-dihydro-2,3-dipyridyl-benzo[*e*]indole (**1**) which possesses two chiral centers. It was anticipated that the reaction would follow a Betti-type reaction[6] and yield a product with only one chiral carbon center, however the formation of **1** was a welcome surprise. As indicated in Scheme 1, substitution of 4-pyridinecarboxaldehyde for 3-pyridinecarboxaldehyde, 4-cyanobenzaldehyde, or 3- cyanobenzaldehyde yields the related compounds *trans*-2,3-dihydro-2-(4′-pyridyl)-3-(3″-pyridyl)benzo[*e*]indole (**2**), *trans*-2,3- dihydro-2-(4′-pyridyl)-3-(4″-cyanophenyl)-benzo[*e*]indole (**3**), and *trans*-2,3- dihydro-2-(4′-pyridyl)-3-(3″-cyanophenyl)benzo[*e*]indole (**4**), respectively. This reaction proceeds with a high degree of stereoselectivity with a *trans*/*cis* ratio of about 98:2 at elevated temperature. IR and ^{1}H NMR spectroscopy and mass spectrometry confirmed their formation. Crystallographic details relating to these compounds as well as information regarding their nonlinear optical responses are presented in Table 1.



Scheme 1.

Pale yellow block crystals of **1** were grown from a toluene solution and crystallized in the noncentrosymmetric space group, $Pca2_1$, with both enantiomeric forms represented in this crystal. Intermolecular hydrogen bonds extend from the NH group to a pyridyl nitrogen atom of a neighboring molecule. The pyridyl group closest to the naphthyl group does not participate in hydrogen bonding. In regard to the packing of the molecules, hydrogen bonding results in the formation of a polymeric chain that extends along a 2_1 axis that lies parallel to the *c* axis (Figure 1).[7] All molecules within a

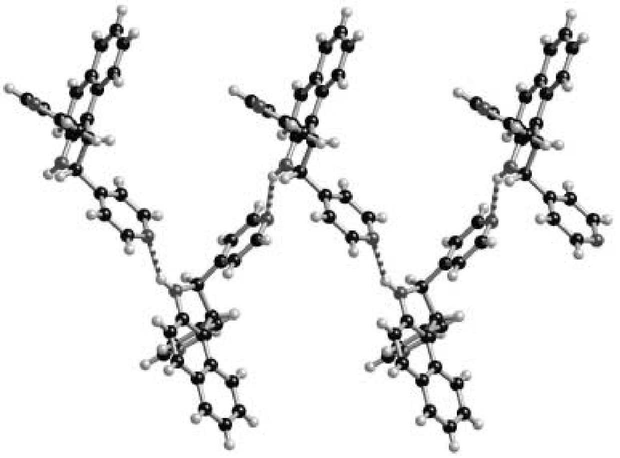


Figure 1. Part of the chiral hydrogen-bonded chain present in crystals of **1**. The chains extend along the *c* axis. Chains of opposite handedness (not shown) are also present in the crystal.

Table 1. Significant crystallographic data, powder SHG activity, and ferroelectric properties for **1**–**5**.[10]

	1	**2**	**3**	**4**	**5**
formula	$C_{22}H_{17}N$	$C_{22}H_{17}N_3$	$C_{24}H_{17}N_3$	$C_{55}H_{42}N_6$	$C_{24}H_{22}N_2O_5$
Fw	323.39	323.39	347.41	786.95	418.44
T [K]	273	273	273	273	273
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinc
space group	$Pca2_1$	$Pca2_1$	$P2_12_12_1$	Cc	$P2_1$
a [Å]	10.671(2)	10.8369(14)	9.0449(16)	30.497(4)	8.562(2)
b [Å]	15.145(3)	15.202(2)	11.4354(19)	11.3416(16)	9.520(2)
c [Å]	9.9724(18)	9.9136(12)	18.083(3)	12.5910(17)	25.861(6)
α[°]	90	90	90	90	90
β[°]	90	90	90	102.291(4)	93.012(5)
γ[°]	90	90	90	90	90
V [Å^3]	1611.6(5)	1633.2(4)	1870.3(5)	4255.2(10)	2104.9(9)
Z	4	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.333	1.315	1.234	1.228	1.320
$\mu(Mo_{K\alpha})$ [cm^{-1}]	0.080	0.079	0.074	0.073	0.093
GOF	0.890	0.904	0.776	0.961	0.803
R_1	0.0528	0.0787	0.0583	0.0532	0.0659
$_wR_2$	0.1354	0.1749	0.1364	0.1403	0.1568
SHG[a]	8.0 U	5.0 U	12.0 U	6.0 U	1.5 U
point group	C_{2v}	C_{2v}	D_2	C_m	C_2
Pr (μC cm^{-2})[b]	~0.17	~0.13	0	~0.12	~0.60

[a] = 1 U = SHG of urea.[b] Pr = remanent polarization.

hydrogen-bonded chain have the same handedness, giving rise to a chiral one-dimensional polymer that has twofold helical character; a right-handed helix is represented in Figure 1. An equal number of symmetry-related chains containing molecules of the opposite handedness are also present in the crystal. The crystal structure of **2** is very similar to that of **1**, as indicated by the similarity of the cell dimensions and space group (Table 1). The packing arrangement is essentially the same, which is not surprising given that the hydrogen-bonding interaction does not involve the 3-pyridyl group.

Crystals of **3** are enantiomerically pure and adopt the chiral space group $P2_12_12_1$. The asymmetric unit consists of one molecule that forms hydrogen bonds to neighbors through the cyano and NH groups. Unlike **1** and **2**, the 4-pyridyl group does not participate in hydrogen bonding. Figure 2 shows the formation of a hydrogen-bonded chain that extends along the b axis. Successive members of the chain are related by a unit cell translation.

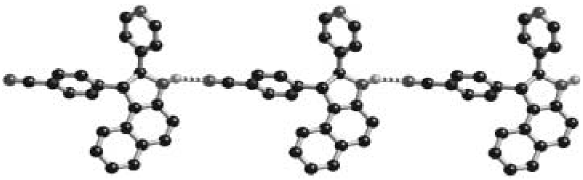


Figure 2. Part of the hydrogen-bonded chain present in crystals of **3**. The chain extends along the b axis with successive molecules related by a unit cell translation. All chains in the crystal are chiral and are of the same handedness.

In crystals of **4**, hydrogen bonding again results in a chain structure but in this case both enantiomeric forms are represented in the one chain as indicated in Figure 3. As with **1** and **2**, it is the 4-pyridyl group that is involved in the hydrogen bonding. Although both enantiomers are present, the space group is again noncentrosymmetric.

A racemic molecular packing arrangement in a noncentrosymmetric or chiral space group is very rare because centrosymmetric packing is very favorable. Four examples illustrate the fact that one molecule bearing both two chiral centers and potential hydrogen-bonding groups has met the requirements of the presence of a highly asymmetric unit and hydrogen-bond orientation effects which are essential for the noncentrosymmetrically polar packing arrangement. This hierarchical crystal engineering strategy is further supported by the following extended example.

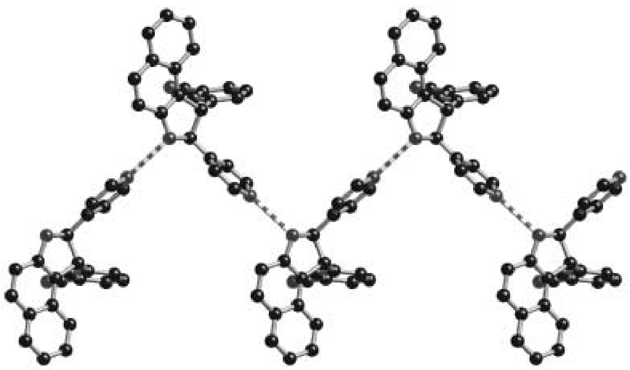


Figure 3. Part of the hydrogen-bonded chain in **4**, which extends along the c axis. The chain is made up of both enantiomers.

The reaction depicted in Scheme 2 was undertaken with a view to providing another example (1-pyridyl-2-ethoxycarbonyl-3-amino-1H-naphtha[2,1-b]pyran-2′-methylacetic acid (**5**)) of crystallization in a noncentrosymmetric space group from a racemic mixture. A single-crystal analysis of the product revealed that the crystals adopt the chiral space group $P2_1$ and that the asymmetric unit contains two unique molecules. We were surprised to discover that the two unique molecules were in fact diastereomers. Figure 4a

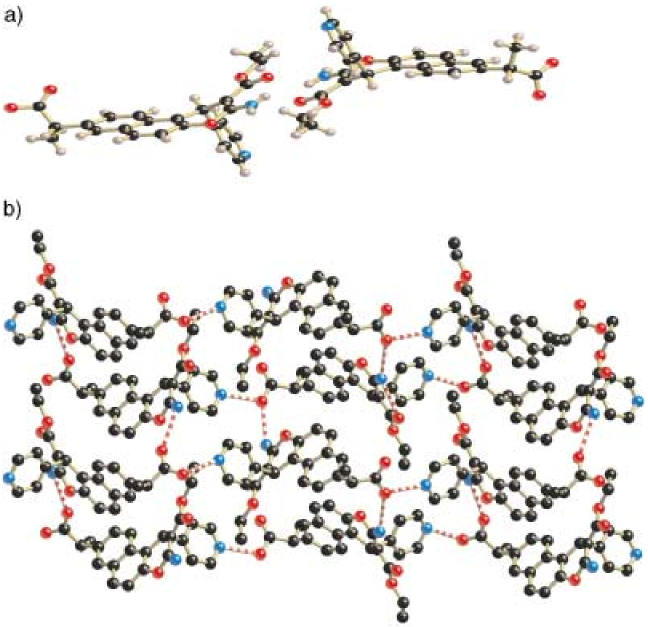
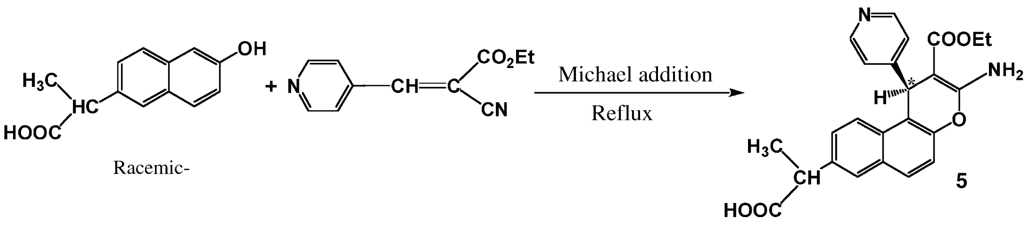


Figure 4. a) The diastereomers (epimers) present in crystals of **5**; b) a 2D hydrogen network formed from both diastereomers. The network extends in the bc plane.



Scheme 2.

shows two unique molecules, which at first glance appear to be almost centrosymmetrically related. Closer inspection reveals that the noncyclic chiral carbon center has the same configuration in both molecules. The fact that the molecules differ in configuration only at one carbon center makes the molecules an epimeric pair. Extensive hydrogen bonding involving both epimers results in a 2D network that extends in the *bc* plane (Figure 4b).

We considered that this series would have an excellent chance of exhibiting NLO effects because the arrangement of the functional groups in these conjugated molecules is likely to result in a significant asymmetric charge distribution that could enhance NLO behavior. Compound **3**, which crystallizes in the chiral space group, $P2_12_12_1$ exhibits the strongest SHG response; approximately 12 times that of urea. Compound **1** has the next strongest response of about eight times that of urea. The very strong response of **3** relative to **1** is probably due to the 4-cyanophenyl group being a better electronic acceptor than the 4-pyridyl group. A similar effect is noted in 4-(4-ethynylphenyl)ethynylbenzonitrile.[4c,8] A weaker but still strong effect is found for **2** (ca. five times that of urea). The difference in NLO behavior found for **1** and **2** is likely to be a consequence of the difference in the electronic effect of 4-pyridyl compared to 3-pyridyl. Compound **4** exhibits a response about six times that of urea.

A powder SHG signal of the order of 1.5 times that of urea was found for **5**. The relative weaker SHG effect may be a consequence of the absence of a suitable donor–acceptor system in the molecule.

In contrast to SHG-active materials which are all noncentrosymmetric, ferroelectric behavior is limited to crystals that belong to one of the 10 polar point groups (C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}). Of the five acentric compounds, **1**, **2**, **4**, and **5** have a polar point group and accordingly they have the potential to display ferroelectric behavior. Experimental results indicate that they are ferroelectrically active compounds. Of particular interest, the electric hysteresis loop of **5** displays typical ferroelectric behavior with a remanent polarization (Pr) of 0.40–0.60 $\mu C\,cm^{-2}$ and coercive field (Ec) of 12 $kV cm^{-1}$ (Figure 5). The saturation spontaneous polarization (Ps) of **5** is about 1.0–3.0 $\mu C\,cm^{-2}$, compared to H-bond type TGS (triglycine sulfate) with a Pr of 3.0 $\mu C\,cm^{-2}$.[9]

In conclusion, the present results provide strong encouragement that crystallization of solutions containing racemic mixtures has the potential to yield noncentrosymmetric products that may have technological applications. At the same time, the present hierarchical crystal engineering methodology, which is based on both two chiral centers and hydrogen bond formation, appears to allow the prediction and control of the noncentrosymmetric polar packing arrangement for racemic molecules, while the molten synthetic technique opens up a new synthetic route for racemic molecules with two chiral centers.

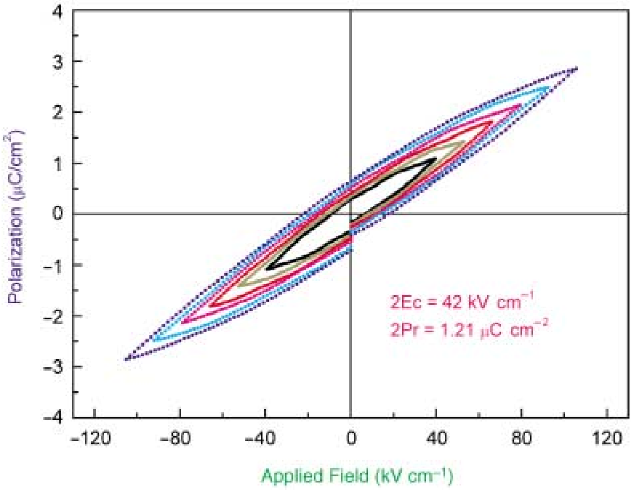


Figure 5. The electric hysteresis loop of **5** as observed by Virtual Ground Mode for a powdered sample in the form of a pellet by using an RT6000 ferroelectric tester at room temperature.

Experimental Section

Synthesis of 1: The molten reaction of 2-naphthol (20 mmol), 4-(aminomethyl)pyridine (20 mmol), and 4-pyridinecarboxaldehyde (23 mmol) at about 180 °C under an N_2 atmosphere afforded racemic *trans*-2,3-dihydro-2,3-di(4′-pyridyl)benzo[*e*]indole (**1**) in 80 % yield (16 mmol) based on 2-naphthol. The ratio of *trans*/*cis* is estimated to be 98:2. IR (KBr): $\tilde{\nu}=$ 3297(m), 3029(w), 2869(w), 1624(m), 1593(s), 1520(m), 1407(m), 1365(m), 1274(m), 1252(m), 1211(m), 1050(w), 994(w), 946(w), 869(w), 819(s), 758(m), 699(m), 610(m), 566(w), 499 cm^{-1} (w); ^1H NMR: $\delta=$ 2.348(br, 1H; NH), 4.519–4.825 (m, 1H; CH), 4.875(d, 1H; CH), 7.019–8.705 (m, 14H; ArH, PyH); MS: *m*/*z*: 323.0.

Synthesis of 2: The procedures are identical to those of **1** except that 3-pyridinecarboxaldehyde was used instead of 4-pyridinecarboxaldehyde. Compound **2** was obtained in 60 % yield based on 2-naphthol. The ratio of *trans*/*cis* is estimated to be 99:1. IR (KBr): $\tilde{\nu}=$3238(s), 3026(w), 1626(m), 1595(s), 1574(m), 1523(m), 1471(m), 1459(m), 1420(m), 1369(m), 1272(w), 1260(w), 1210(m),1155(w),1126(w), 995(w), 927(w), 851(m), 808(s), 771(m), 745(m), 715(m), 654(w), 634(w),603(w), 553 , cm^{-1} (w); MS: *m*/*z*: 323.0.

Synthesis of 3: The procedures are identical to those of **1** except that 4-cyanobenzoaldehyde was used in place of 4-pyridinecarboxaldehyde. Compound **3** was obtained in 75 % yield based on 2-naphthol. The ratio of *trans*/*cis* is estimated to be 99:1. IR (KBr): $\tilde{\nu}=$3341(s), 3053(w), 2868(w), 2231(m), 1625(m), 1593(s), 1521(m), 1469(m), 1412(m), 1363(m), 1250(m), 1208(w), 1252(m), 1178(m), 1111(w), 992(w), 949(w), 868(w), 823(s), 753(m), 695(m), 606(m), 569 cm^{-1} (w); MS: *m*/*z*: 347.0.

Synthesis of 4: The procedures are identical to those of **1** except that 3-cyanobenzoaldehyde was used to replace 4-pyridinecarboxaldehyde. Compound **4** was obtained in 60 % yield based on 2-naphthol. The ratio of *trans*/*cis* is estimated to be 99:1. IR (KBr): $\tilde{\nu}=$3321(m), 3056(w), 2231(m), 1626(m), 1596(s), 1521(m), 1469(w), 1451(m), 1412(m), 1365(m), 1263(m), 1251(m), 1155(m), 1063(w), 992(w), 903(w), 858(w), 807(s), 743(m), 693(m), 655(w), 616(w), 549(m), 518 cm^{-1} (w); MS: *m*/*z*: 347.0.

Synthesis of 5: Piperidine (0.6 mL) was added to a stirred mixture of racemic (or (*S*))-6-hydroxy-2′-methyl-2-naphthaleneacetic acid (10 mmol) and ethyl-2-cyano-1-(4′pyridyl)acrylic acetate (10 mmol) in ethanol (20 mL). The mixture was refluxed for 24 h. The orange solution was poured into ice water (100 ml). The resulting precipitate was isolated by filtration, washed with water, dried, and recrystallized from ethanol. The colorless needles of **5** were obtained in about 84 % yield (8.37 mmol). IR (KBr): $\tilde{\nu}=$3433(m), 3302(w), 2977(w), 2930(w), 1717(w), 1680(s), 1621(m), 1603(m), 1526(s), 1472(m), 1407(w), 1306(w), 1283(w), 1225(s), 1196(w), 1068(m), 1034(w), 833(w), 816(w), 785(w), 651(w), 527 cm^{-1} (w).

Acknowledgement

This work was supported by The Major State Basic Research Development Program (Grant No.G2000077500), Distinguished Young Scholar Fund to R.-G. Xiong and Z. Xue from NSFC (No.20225103 and No. 20028101), the National Natural Science Foundation of China (BK2003204 20030284001(SRFDP)), and the National Science Foundation of the USA (CHE-9904338).

---

[1] a) K. T. Holman, A. M. Pivovar, M. D. Ward, *Science* **2001**, *294*, 1907; b) M. D. Hollingsworth, *Science* **2002**, *295*, 2410; c) V. R. Thalladi, S. Brasselet, H. C. Weiss, D. Blaser, A. K. Katz, H. L. Carrell, R. Boese, J. Zyss, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1998**, *120*, 2563; d) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375; e) J. Zyss, S. Brasselet, V. R. Thalladi, G. R. Desiraju, *J. Chem. Phys.* **1998**, *109*, 658; f) V. R. Thalladi, R. Boese, S. Brasselet, I. Ledox, J. Zyss, R. K. R. Jetti, G. R. Desiraju, *Chem. Commun.* **1999**, 1639.

[2] a) J. Zyss, D. S. Chemla in *Nonlinear Optical properties of Organic Molecules and Crystals, Vol. 1*, Academic Press, New York, **1989**, p .23; b) N. J. Long, *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21; c) J. Zyss, J. F. Nicoud, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 533; d) M. C. Etter, K. S. Huang, *Chem. Mater.* **1992**, *4*, 824; e) D. Y. Curtin, C. Paul *Chem. Rev.* **1981**, *81*, 525; f) *Nonlinear Optical Effects and Materials, Vol. 72* (Ed.: P. Gunter), Springer, Berlin, Germany, **2000**.

[3] a) M. S. Wong, C. Bosshard, P. Gunter, *Adv. Mater.* **1997**, *9*, 837; b) C. Jiank, T. G. Schairmann, P. Albrecht, F. Marlow, R. Macdonald, *J. Am. Chem. Soc.* **1996**, *118*, 6307; c) H. Zhang, X. M. Wang, K. C. Zhang, B. K. Teo, *Coord. Chem. Rev.* **1999**, *183*, 157; d) R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem.* **1999**, *111*, 557; *Angew. Chem. Int. Ed.* **1999**, *38*, 536; e) Z.-F. Chen, R.-G. Xiong, B. F. Abrahams, X.-Z. You, C.-M. Che, *J. Chem. Soc. Dalton Trans.* **2001**, 2453; for ferroelectric compounds: f) H. N. Lee, D. Hesse, N. Zakharov, U. Gosele, *Science* **2002**, *296*, 2006; g) A. V. Bune, V. M. Fridkin, S. Duchame, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin, A. Zlatkin, *Nature* 1998, **391**, 874; h) M. Szafranski, A. Katrusiak, G. J. McLntyre, *Phys. Rev. Lett.* **2002**, *89*, 215507–215501.

[4] a) R-. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams, Z. Xue, *Angew. Chem.* **2002**, *114*, 3954; *Angew. Chem. Int. Ed.* **2002**, *41*, 3800; b) O. Teichert, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2196; c) M. Ohkita, T. Suzuki, K. Nakatani, T. Tsuji, *Chem. Commun.* **2001**, 1454; d) R. W. Saalfrank, H, Maid, F. Hampel, K. Peters, *Eur. J. Inorg. Chem.* **1999**, 1859; e) P. Gangopadhyay, T. P. Radhakrishnan, *Angew. Chem.* **2001**, *113*, 2517; *Angew. Chem. Int. Ed.* **2001**, *40*, 2451; f) V. R. Thalladi, R. Boese, S. Brasselet, I. Ledoux, J. Zyss, R. K. R. Jetti, G. R. Desiraju, *Chem. Commun.* **1999**, 1639.

[5] C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1991**, *113*, 9811.

[6] a) M. Betti, *Gazz. Chim. Ital.* **1990**, *30*, 310; b) M. Betti, *Gazz. Chim. Ital.* **1901**, *31*, 377; c) M. Betti, *Gazz. Chim. Ital.* **1901**, *31*,191; d) Betti, M. , E. Lucchi, *Boll. Sci. Fac. Chim. Ind. Bologna*, **1940**, *1–2*, 2.

[7] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**; b) G. R. Desiraju, T. Steiner, *The weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**; c) M. J. Calhorda, *Chem. Commun.* **2000**, 801.

[8] a) P. J. Langley, J. Hulliger, R. Thaimattam, G. R. Desiraju, *New J. Chem.* **1998**, *22* 1307; b) G. R. Desiraju, R. L. Harlow, *J. Am. Chem. Soc.* **1998**, *120*, 6757.

[9] a) W. H. Baur, *Acta Crystallogr. Sect. B* **1982**, *B24*, 1968; b) B. C. Frazer, R. Peninsky, *Acta Crystallogr.* **1967**, *23*, 1948; c) S. K. Kurtz, T. T. Perry, *J. Appl. Phys.*.**1968**, *39*, 3798; d) S. Hoshino, Y. Okaya, R. Peninsky, *Phys. Rev.* **1959**, *115*, 323; e) S. R. Fletcher, E. T. Keve, A. C. Skapski, *Ferroelectrics* **1976**, *14*, 789; f) X. Solans, F. Franco, C. Miravitlles, *Ferroelectrics* **1985**, *62*, 59.

[10] The structures were solved with direct methods using the program SHELXTL (Sheldrick, **1997**).[11] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. CCDC-191834, and CCDC-210948–210951 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

[11] G. M. Sheldrick, (**1997**). SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA.

Received: May 30, 2003
Revised: January 7, 2004 [F5425]