

Conserved Hydrogen Bonded Tartrate Frameworks: Inclusion of Amines and Implications for Second Harmonic Generation

RENUKA KADIRVELRAJ¹, SANTANU BHATTACHARYA,² and
TAYUR N. GURU ROW^{1,2,*}

¹*Solid State and Structural Chemistry Unit and* ²*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India.*

(Received: 21 January 1997; in final form: 12 June 1997)

Abstract. A series of anilinium cations with various functional groups as substituents has been chosen to form salts with L-tartaric acid and D-dibenzoyl tartaric acid. The salts show second harmonic generation activities comparable to urea. The tartrate frameworks provide conformationally rigid hydrogen bonded frameworks for the incorporation of these cations. The SHG activity of these salts appear to depend upon the type of framework provided by the tartrate anions, which in turn decides the orientation of the cations.

Key words: supramolecular chemistry, hydrogen bonding, second harmonic generation, anionic framework.

1. Introduction

The construction of multimolecular hydrogen bonded templates with preconceived physico-chemical properties in the solid state is one of the key conundrums of present day materials science. This addresses problems like the design and construction of molecular metals [1], ferromagnets [2] and self-assembling ensembles for catalytic applications [3] etc. However, the approaches to the production of such structurally controlled assemblies are complicated due to the large number of conformations the individual molecules (blocks) in these ensembles tend to adopt. The way in which these blocks assemble depend largely on the intermolecular interactions between them. During the last few years, halogen-halogen interactions [4], hydrogen bonding [5] and other noncovalent forces [6] have been used to provide predictable frameworks for organized self-assembly. Hydrogen bonding [7] between molecular entities is by far the most well understood interaction for the effective tailoring of supramolecular arrays. Due to its multidirectional nature, hydrogen bonding is an useful tool in crystal engineering [8]. In particular, networks built on hydrogen tartrates and polarizable cations have received consid-

* Author for correspondence. Fax: 91-080-3311310; e-mail: sscting@sscu.iisc.ernet.in

erable attention in the fabrication of well-developed transparent crystals for second harmonic generation.

Tartaric acid [9] is capable of initiating multidirectional hydrogen bonding and hydrogen bonded monohydrogen tartrates have been shown to form frameworks for cationic incorporation [10–14]. Such frameworks can be used to orient the net dipoles of a set of ions, molecules or molecular assemblies in a crystal in a particular direction leading to good NLO properties. Several groups have worked on the approach of combining organic polarizable cations with hydrogen bonding organic (or inorganic) anions to produce novel materials that show SHG [10–14]. We have synthesized and solved the crystal structures of a series of binary salts of tartrate and dibenzoyl tartrate anions with polarizable cations [10, 14]. Since the maximization of SHG depends on the optimum orientation of the charge transfer axis of the molecule with the crystallographic axis [15], our chosen range of a series of anilinium cations have helped us to examine the efficiency of this alignment of dipoles and to decipher the role played by the anionic network in these systems and its influence on the SHG activity shown by the salts [14].

2. Experimental

All the amines used were purified by distillation under reduced pressure. L-tartaric acid and D-dibenzoyl tartaric acid were obtained from Sigma. The salts were prepared by dissolving equimolar amounts of the corresponding acid and the respective base in methanol–water mixture. The resulting mixture was stirred and left to evaporate to near dryness at room temperature. The crystals which formed were filtered off, recrystallized twice from methanol–water mixture, filtered and dried. Melting points were examined in open capillaries and are uncorrected.

In the L-tartrate salt series, anilines with the carboxylic acid group as substituent (2-carboxylic acid, 3-carboxylic acid and 4-carboxylic acid aniline) resisted binary salt formation. This was true irrespective of the location of the carboxyl substituent in the aniline moiety. Anilines with carboxyl substituent are zwitterionic in nature and the amino function in these bases are protonated. Therefore, they cannot deprotonate a tartaric acid molecule. It is interesting to note that analogous L-tartrate salts could not be prepared with pyridine carboxylic acid either [10b]. In contrast, haloanilinium salts (entries 1–6, Table I) could be prepared easily irrespective of the nature and location of the halogen substituent on the aromatic ring. All toluidines and xylidines (entries 9–13, Table I) smoothly formed corresponding salts with L-tartaric acid. Anilines, like their pyridine counterparts, when substituted with electron withdrawing groups resisted salt formation. Thus, placing a nitro group at the *ortho*, *meta* or *para* position (2-nitro, 3-nitro, 4-nitro aniline) relative to the amino group of the corresponding anilines prevented salt formation. Similarly, 3,5-dinitro aniline and 4-bromo-2,6-dimethyl aniline did not form salts with L-tartaric acid.

Table I. Physical characteristics of anilinium-l-tartrate salts and measured powder SHG intensities.

Entry	Base (melting point in °)	Melting point of L-tartrate salt	SHG of salt (with reference to urea)
1	3-fluoro (186 - b.p)	173	1
2	2-chloro (-14)	143	1
3	3-chloro(-10)	148-150	1
4	4-chloro (70-71)	171-172	1
5	3-bromo (16.8)	168-169	1
6	4-iodo (67-68)	154	0.9
7	3-methoxy (< -10)	152	nil
8	4-methoxy (57)	182-184	+*
9	2-methyl (-28)	159	+*
10	3-methyl (-50)	148	+*
11	4-methyl (44-45)	186-188	1.2
12	2,3-dimethyl (2.5)	169-170	+*
13	2,6-dimethyl	147	0.75

* Not measured quantitatively.

The formation of the salts was characterized by X-ray powder diffraction studies on a STOE STADI-P diffractometer. Figure 1 shows a representative example of the patterns of L-tartaric acid, 4-toluidine, 4-toluidinium-L-monohydrogen tartrate and a physical mixture of the acid and amine respectively. The crystal structures of the salts (entries 1-9, Table II; entries 1-4, Table III) were solved by direct methods using SHELX86 [16] and refined using SHELXS76 [17a] and SHELXL93 [17b].

The SHG intensities of the salts were measured using the standard powder technique [1] on a polycrystalline sample ground to uniform grain size. Radiation (1.060 μm) from a pulsed Q-switched Nd:YAG laser (Quanta Ray, DCR-2A) with a pulse duration of 8 ns was used to generate second harmonic signals from the samples. The forward scattered SHG signals were collected using collection optics and passed through a filter which transmits only 532 nm radiation. The intensities of the incident laser beam and the SHG radiation were measured using an energy ratio meter (LPC RJ-7620) equipped with pyroelectric (LPC RJP-735) and silicon (LPC RJP-765) detectors. The measured SHG intensities of the samples were normalized with respect to that of urea.

3. Results and Discussion

In all these structures, the anions are used as building blocks while the cations incorporated between layers of anions provide well directed hydrogen bonding patterns. However, the cations have a tendency to pack antiparallel to each other, most often generating a center of symmetry, though the individual cationic

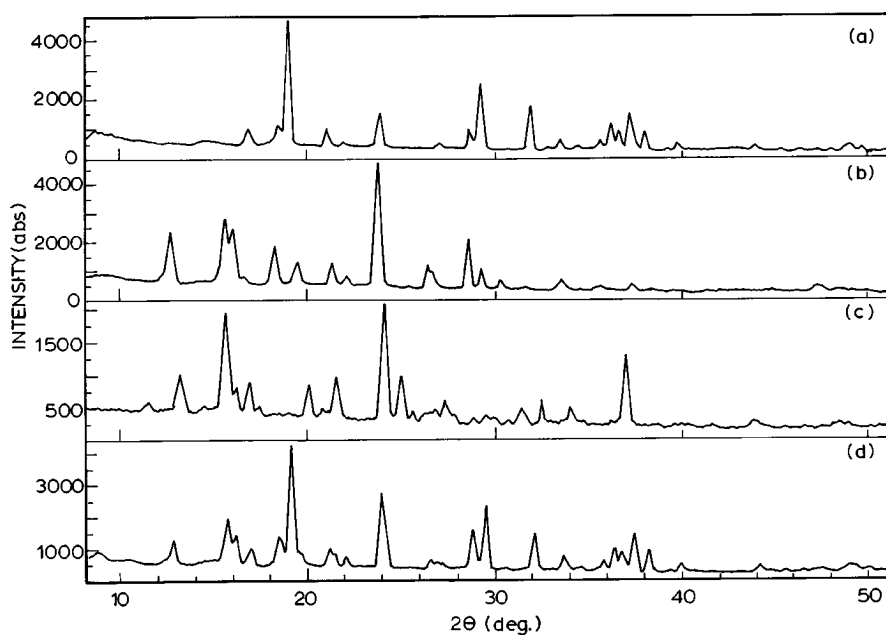


Figure 1. Powder X-ray patterns of L-tartaric acid (a), 4-toluidine (b), 4-toluidinium-L-monohydrogen tartrate(c) and a physical mixture of the acid and amine (d), respectively.

Table II. Cationic counterpart and SHG activity in D-dibenzoyl tartrate structures.

Entry	Base	SHG of salt (with reference to urea)
1	2,3-xylylidine	0.8
2	2,6-xylylidine	0.9
3	2-toluidine	nil
4	3-toluidine ^a	0.9
5	3-toluidine ^b	0.9
6	1,4-diamino butane	faint ^c
7	3-fluoroaniline	faint ^c
8	1-nonylamine	faint ^c
9	1-decylamine	faint ^c

^{a,b} Stoichiometric variants of acid and amine (1 : 1 and 1 : 2).

^c SHG activity comparable to quartz.

molecular hyperpolarizability might be large. The anionic framework in tartrates and dibenzoyl tartrates is thus used to reorient these cationic moieties in optimum orientation for maximum SHG.

Table III. Inter-layer separation d , θ and SHG values for tartrate salts belonging to Type I.

Entry	Structure	d	θ	SHG [urea (*) or quartz (#) as reference]
1	3-anisidinium hydrogen-L-tartrate hydrate [14a]	10.2	0.0	nil
2	4-toluidinium hydrogen-L-tartrate hydrate [14a]	9.9	2.96	1.2*
3	2,6-xylidinium hydrogen-L-tartrate hydrate [14b]	10.1	4.56	0.8*
4	3-bromoanilinium hydrogen-L-tartrate [14c]	10.5	0.0	1#
5	1-imidazolium hydrogen-L-tartrate [12c]	10.9	9.11	+
6	1-benzimidazolium hydrogen-L-tartrate [12e]	10.9	0.0	+

+ Data not available.

We present here a study of the influence of the conformation of the individual tartrate building block on the stability of the anionic framework and its correlation with the SHG. The general characteristics for the formation of a stable framework are as follows. Each individual component (block) of the framework should have the capacity to link to the adjacent block through well-directed interactions like hydrogen bonding. These links should be subtle enough to allow the incorporation of the cations (or anions as the case maybe) between the strands forming the network and strong enough to prevent the breakdown of the network during this incorporation. The monovalent tartrate anions in these salts can form layered, two-dimensional networks through hydrogen bonding. These tartrate moieties are the building blocks of the network. Infinite chains are formed in a ‘head-to-tail’ fashion between the carboxylate end of an anion and the carboxylic acid end of an adjacent anion through well-directed O—H \cdots O hydrogen bonds of ~ 2.5 Å. The hydroxyl groups, present at almost right angles to the infinite chain direction in the tartrate anion, crosslink adjacent anionic chains. The framework thus formed, allows the incorporation of the cations. These act as cross-links between adjacent anionic strands and layers through hydrogen bonding, thus completing the three-dimensional supramolecular network. This leads to the stable frameworks formed by tartrate and substituted tartrate units.

Basically, these salts fall into three categories. Type I has individual tartrate units linked through strong O—H \cdots O hydrogen bonds of ~ 2.5 Å which is referred to as the inter-block separation. This generates an infinite chain of tartrate units in the lattice. The cations are incorporated between adjacent strands of these chains, holding them together by hydrogen bonding. The distance between the strands is referred to as the inter-strand separation. This distance depends on the size, shape and orientation of the cation and is therefore variable. This molecular assembly repeats in layers in the crystal lattice, thus generating a robust, three-dimensional topography. The distance between the layers is referred to as the inter-layer separation, d (Figure 2). The infinite chains in Type I structures run parallel or nearly

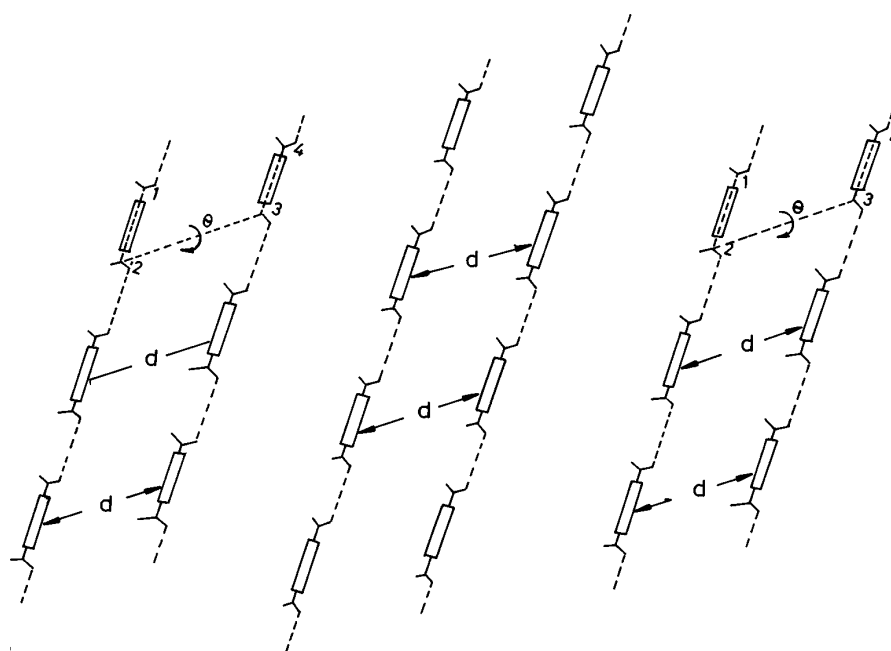


Figure 2. Definition of d and θ .

parallel to each other. The inter-layer separation is $\sim 10 \text{ \AA}$ irrespective of the size, charge and nature of the cation (Tables III, IV) Since the inter-block and inter-layer separation are invariant, the framework in Type I structures is conformationally rigid.

Type II structures have the infinite chain motif in the crystal lattice as in Type I. But the chains are no longer parallel to each other (Table V). The variable alignment of the chains do not allow an invariant inter-layer separation as in Type I.

Type III does not have the $\text{COO}^- - \text{HOOC}$ kind of hydrogen bonding which is present in the other two categories. If there are solvent water molecules in the network, the carboxylic ends of the anions twist to form localized hydrogen bonding with the cation and the solvent [14b, c] preventing the formation of the infinite chain motif.

With the loss of links between the individual anionic units, the formation of the framework is disrupted. Also, in cases where there is a doubly deprotonated anion, an infinite chain may develop through hydrogen bonding between the carboxylate end of the anion and the hydroxyl group of the neighboring anion [12f, 20]. Thus, the presence of solvent molecules recast the packing modes and the hydrogen bonding patterns. These Type III structures have no hydrogen bonded network but this does not seem to have a direct bearing on the SHG activity [14b, c].

In Type I, the inter-layer separation, d is plotted against the torsion angle, θ which corresponds to the atoms 1–2–3–4 (Figure 3). In cases where there are two

Table IV. Inter-layer separation d , θ and SHG values for dibenzoyl tartrate salts belonging to Type I.

Entry	Structure	d	θ	SHG [urea (*) or quartz (#) as reference]
1	2,3-xylidinium hydrogen-D-dibenzoyl tartrate hydrate [14b]	10.4	2.29	0.8*
2	2,6-xylidinium hydrogen-D-dibenzoyl tartrate [14b]	10.3	4.86	0.9*
3	2-toluidinium hydrogen-D-dibenzoyl tartrate [14b]	10.6	5.8	nil ⁺
4	3-toluidinium hydrogen-D-dibenzoyl tartrate [14b]	10.3	7.18	0.9*
5	3-fluoro anilinium hydrogen-D-dibenzoyl tartrate [14c]	10.4	0.08	1#
6	1-nonylammonium hydrogen-D-dibenzoyl tartrate [14c]	10.7	0.87	1#
7	1-decylammonium hydrogen-D-dibenzoyl tartrate [14c]	10.4	8.58	1#

⁺ Space group is $P2_12_12_1$.

Table V. Torsion angle θ between infinite chains and the SHG activity in tartrate and dibenzoyl tartrate structures belonging to Type II.

Entry	Structure	SHG [urea (*) or quartz (#) as reference]	Angle ($^\circ$)
1	Guanidinium hydrogen-L-tartrate hydrate [13b]	1*	130.5
2	1-phenyl ethyl ammonium hydrogen-L-tartrate [19]	1#	42.18
3	Piperazinium-bis hydrogen-L-tartrate [12b]	1.6#	106.48
4	2-amino-5-nitropyridinium hydrogen-L-tartrate [13a]	3.2*	117.43

molecules in the asymmetric unit, the average values of d and θ have been used. This polar plot of d versus θ clearly shows the tartrate and dibenzoyl tartrate salts of Type I clustering together, indicating the overall rigidity of the framework. Also, the conservation of the conformation of the individual dibenzoyl monohydrogen tartrate anions in the salts (Figure 4) lends support to this rigidity. This preferential value of θ clearly represents the invariant nature of the tartrate framework. Figure 5 shows a representative example of inter-layer separation in 3-toluidinium-D-dibenzoyl monohydrogen tartrate (1 : 1) [14b]. As shown in Tables III and IV, the SHG value of the Type I compounds do not exceed the SHG of the framework. (L-tartaric or D-dibenzoyl tartaric acid) which is comparable to urea. The small variation in the quantitative value of SHG in these compounds may be due to differences in packing modes, particle size, phase matching etc. Nevertheless, the

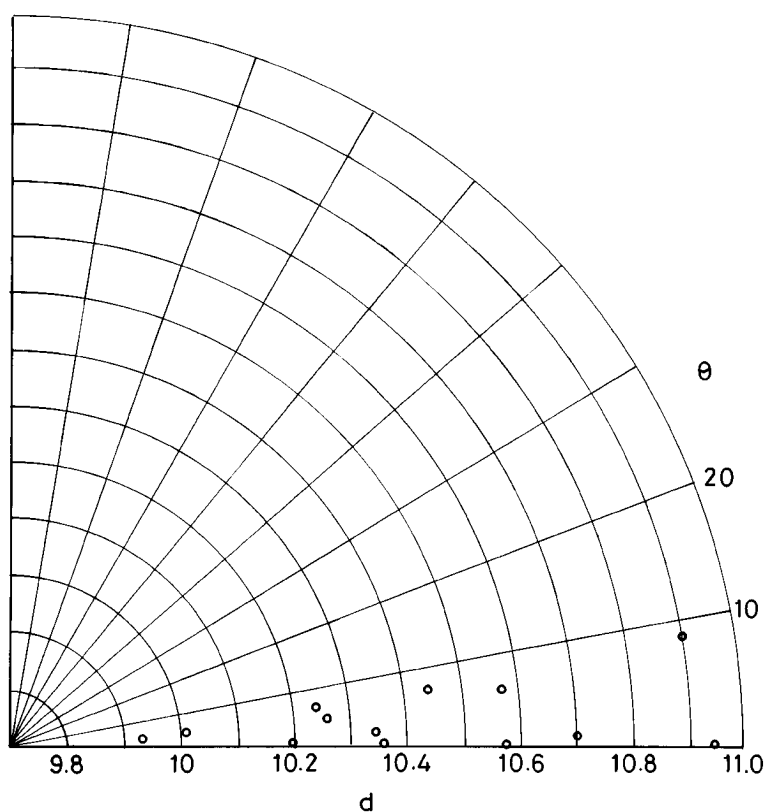


Figure 3. Correlation plot of d versus θ in Type I tartrate and dibenzoyl tartrate salts.

maximum value of SHG is restricted to that of the framework. We believe that this remarkable finding suggests directives towards the design of future NLO materials based on fixed frameworks.

Interestingly, the large NLO response in 2-amino-5-nitropyridinium hydrogen L-tartrate [13a] is strongly influenced by the nature of the cations and they pack parallel to each other in this structure. This compound belongs to the Type II category and the polar geometry could be due to the flexible nature of the tartrate host matrix which induces the cation influenced nonlinear optical response.

Hence the cation packing modes, though important, depend entirely on the nature of the anionic framework. It could be that the small changes in the NLO response of Type I structures is also a measure of a weak departure from centrosymmetry of the cation sublattice. However, the powder SHG test is a semi-qualitative method and only indicative of trends [13a].

In summary, the Type I structures which statistically predominate the hydrogen bonded tartrate framework structures known so far have their SHG values restricted to that of the spacer units that build up the network. The incorporation of cations

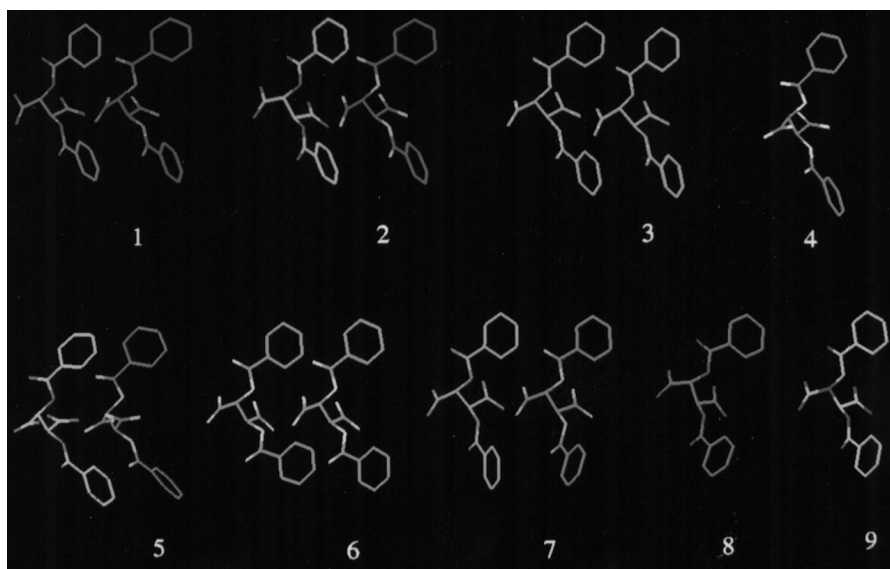


Figure 4. Anionic conformation in dibenzoyl tartrate salts with different cations. (1) 2,3-xylylidinium; (2) 2,6-xylylidinium; (3) 3-toluidinium (1 : 1); (4) 1,3-diamino butanium; (5) 3-toluidinium (1 : 2); (6) 2-toluidinium; (7) 3-fluoro anilinium (8) 1-nonyl ammonium; (9) 1-decyl ammonium.

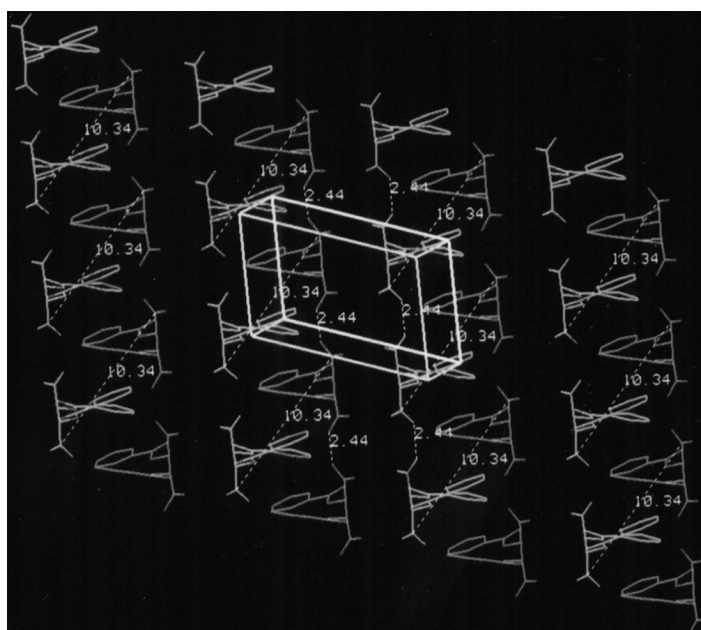


Figure 5. Representative example – inter-block and inter-layer distances in 3-toluidinium-D-dibenzoyl monohydrogen tartrate (1 : 1).

with reasonably large molecular hyperpolarizabilities into these networks would not lead to materials with large SHG intensities. It is clear from the few examples of Type II structures that the flexibility in the framework could enhance the SHG, leading to more efficient materials. One can also explore noncovalent interactions other than hydrogen bonding between molecular entities for effective maximization of the SHG response.

Acknowledgements

We thank Drs. C.K Subramanian and B.R. Prasad, Department of Physics, IISc for help in SHG measurements and the Department of Science and Technology, India for financial support.

References

1. T. J. Marks: *Angew. Chem. Ed. Engl.* **29**, 857 (1990) and references therein.
2. J. S. Miller and A. J. Epstein: *Angew. Chem.* **106**, 399 (1994).
3. G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, and D. M. Gordon: *Acc. Chem. Res.* **28**, 37 (1995) and references therein.
4. (a) V. A. Kumar, N. S. Begum, and K. Venkatesan: *J. Chem. Soc., Perkin Trans 2*, 463 (1993). (b) G. R. Desiraju and R. Parthasarathy: *J. Am. Chem. Soc.* **111**, 8725 (1989).
5. (a) J. Bernstein, R. E. Davis, L. Shimoni, and N.-L. Chang: *Angew. Chem. Int. Ed. Engl.* **34**, 1555 (1995) and references therein. (b) C. B. Aakeröy and K. R. Seddon: *Chem. Soc. Rev.* 397 (1993) and references therein. (c) M. C. Etter: *J. Phys. Chem.* **95**, 4601 (1991).
6. J. C. Macdonald and G. M. Whitesides: *Chem. Rev.* **94**, 2383 (1994) and references therein.
7. (a) W. M. Latimer and W. H. Rodebush: *J. Am. Chem. Soc.* **42**, 1419 (1920). (b) G. C. Pimentel and A. L. McClellan: *The Hydrogen Bond*, Freeman, San Francisco (1960) and references therein.
8. J. P. Mathias, and J. F. Stoddart: *Chem. Soc. Rev.* **21**, 215 (1992) and references therein.
9. Y. Okaya, N. R. Stemple, and M. I. Kay: *Acta Crystallogr.* **21**, 237 (1966).
10. (a) Bhattacharya, P. Dastidar and T. N. Guru Row: *Chem. Mater.* **6**, 531 (1994). (b) P. Dastidar, T. N. Guru Row, B. R. Prasad, C. K. Subramanian, and S. Bhattacharya: *J. Chem. Soc., Perkin Trans. 2* **12**, 2419 (1993).
11. O. Watanabe, T. Noritake, Y. Hirose, A. Okada, and T. Kurauchi: *J. Mater. Chem.* **3**, 1053 (1993).
12. (a) C. B. Aakeröy and M. Nieuwenhuyzen: *J. Am. Chem. Soc.* **116**, 10983 (1994). (b) C. B. Aakeröy, G. S. Bahra, P. B. Hitchcock, Y. Patell, and K. R. Seddon: *J. Chem. Soc., Chem. Commun.* 553 (1992). (c) C. B. Aakeröy and P. B. Hitchcock: *J. Mater. Chem.* **3**, 1129 (1993). (d) C. B. Aakeröy, G. S. Bahra, P. B. Hitchcock, Y. Patell, and K. R. Seddon: *J. Chem. Soc., Chem. Commun.* 1856 (1989). (e) C. B. Aakeröy, P. B. Hitchcock: *Acta Crystallogr.* **C50**, 759 (1994). (f) C. B. Aakeröy, G. S. Bahra, and M. Nieuwenhuyzen: *Acta Crystallogr.* **C52**, 1471 (1996).
13. (a) J. Zyss, R. Masse, M. Bagieu-Bucher, and J.-P. Levy: *Adv. Mater. Sci.* **5**, 120 (1993). (b) J. Zyss, J. Pecaut, J.-P. Levy, and R. Masse: *Acta Crystallogr.* **B49**, 334 (1993). (c) R. Masse, M. Bagieu-Bucher, J. Pecaut, J.-P. Levy, and J. Zyss: *Nonlinear Optics* **5**, 413 (1993).
14. (a) K. Renuka, T. N. Guru Row, B. R. Prasad, C. K. Subramanian, and S. Bhattacharya: *New J. Chem.* **19**, 83 (1995). (b) R. Kadirvelraj, A. M. Umarji, W. T. Robinson, S. Bhattacharya, and T. N. Guru Row: *Chem. Mater.* **8**, 2313 (1996). (c) R. Kadirvelraj, S. Bhattacharya, and T. N. Guru Row: *New J. Chem.* **20**, 1165 (1996).
15. J. Zyss and J. L. Oudar: *Phys. Rev.* **A26**, 2028 (1982).
16. G. M. Sheldrick: *SHELXS86 Program for Crystal Structure Solution*, Göttingen University, Germany (1986).
17. (a) G. M. Sheldrick: *SHELXS76 Program for Crystal Structure Determinations*, University of Cambridge, England (1976). (b) G. M. Sheldrick: *SHELXS86 Program for Crystal Structure Refinement*, Göttingen University, Germany (1993).

18. S. K. Kurtz and T. T. Perry: *J. Appl. Phys.* **39**, 3798 (1968).
19. E. Molins, C. Miravittles, F. Lopez-Calahorra, J. Castells and J. Raventos: *Acta Crystallogr.* **C45**, 104 (1989).
20. W. Krumbe, S. Haussuhl, and R. Fröhlich: *Z. Kristallogr.* **187**, 309 (1989).