

# Hydrogen and fluorine in crystal engineering: systematics from crystallographic studies of hydrogen bonded tartrate–amine complexes and fluoro-substituted coumarins, styrylcoumarins and butadienes

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## Abstract

Three aspects of crystal engineering in molecular crystals are presented to emphasize the role of intermolecular interactions and factors influencing crystal packing. Hydrogen bonded

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tartrate–amine complexes have been analyzed with the propensity for formation of multidirectional hydrogen bonding as a key design element in the generation of materials for second harmonic generation (SHG). The invariance of the framework in DBT and its possible implications on SHG is outlined. The role of Fluorine in orienting molecules of coumarins, styrylcoumarins and butadienes for photodimerization is described with particular emphasis on its steering capability. Usage of coumarin as an design element for the generation of polymorphs of substituted styrylcoumarins is examined with specific examples. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Crystal engineering; Tartrate–amine complexes; Structure and SHG; Organic fluorine; Coumarin addition

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## 1. Introduction

The understanding of the packing in crystalline lattices and the subsequent generation of engineered interactions between preselected constituent blocks in these resulting assemblies form the basis of modern day crystal engineering. Interestingly, there is as yet no generally successful approach to predict, let alone control molecular orientations in crystals. Thus, the rational design and preparation of new materials for specific applications is still at an evolutionary stage and the focus is mainly on understanding factors that determine crystal packing. Any approach which ensures a particular packing mode would generate a tool for engineering supramolecular assemblies [1]. In crystal structures the packing of the molecules mainly depend on the symmetry of the lattice and the ensuing intermolecular interactions [2] which drive the molecules to assemble together. Several types of steering forces have been recognized during the last few years which generate well organized extended structures. Some of them are halogen–halogen interactions [3,4], charge transfer [5], electrostatic forces [6–8],  $\pi$ – $\pi$  stacks [9,10], non-covalent interactions in guest host complexes [11,12] and molecular self assembly [13–16]. The structures thus generated using these tools are molecular crystals [17,18], liquid crystals [19,20], colloids [21], micelles [22,23], emulsions [24], phase separated polymers [25,26], Langmuir–Blodgett films [27] and self assembled monolayers [28,29].

The most decisive instrument in crystal engineering [30,31] so far is the use of hydrogen bonding as a steering force. The utility of hydrogen bonded motifs in the generation of new materials have been extensively reviewed [32–47]. The ability of the hydrogen bonds, in particular, to orient polarizable cations in hydrogen bonded networks of anions has paved the way for the synthesis of a large number of materials for nonlinear optics [48–70] as these networks lead to non-centrosymmetric crystals for second harmonic generation.

Fluorine, the smallest and the most electronegative element among the halogens, provides another design tool in crystal engineering to steer molecules into preconceived orientations [71–79]. Recent Cambridge Structural Database (CSD) [80]

analyses have shown that covalently-bound fluorine (in contrast to anionic fluoride) does not generally act as a hydrogen bond acceptor [81,82]. The larger halogens (Cl, Br and I) have been successfully used to steer molecules of coumarin into desirable orientations for 2 + 2 photodimerization reactions. Fluorine on the other hand, does not behave in the same way and hence the a priori predictability of the steering capability cannot be deduced based on results from analogous compounds containing other halogen atoms.

A systematic crystallographic study of both hydrogen bonded systems for nonlinear optics and fluoro derivatives of several organic materials would provide insights into the operative details of the resulting engineered interactions and this review relate primarily to the results obtained on a number of structures obtained from single crystal diffraction studies.

## 2. Hydrogen bond as a design element

The conventional design element in organic chemistry has always been the stable and well directed covalent bond which results in fabricated structures. Hydrogen bond usage now has also become an useful design element in arranging molecules in the solid state. The work of Etter and co-workers has immensely contributed to the understanding of both stable and well directed preferences in hydrogen bonds. Structures of amides, diarylurea, imides, carboxylic acids, nitroanilines, aminopyrimidines and guanidinium sulfonates are some of the examples involving hydrogen bonded networks [83–88]. Molecular tapes and ribbons to generate supramolecular structures in melamines and cyanuric acids [32] have demonstrated the versatility of hydrogen bonding. Design of self complementary hydrogen bonded 2-D networks [89], co-crystals from self assemblies of dicarboxylic acids [90] and formation of cyclic arrays [91] via hydrogen bonded motifs are clear indicators of the flexibility in the design features. Some of these assemblies have symmetry elements in the crystal lattice aiding the formation of the motifs containing the hydrogen bonds. Most of the supramolecular aggregation is also through the symmetry relations in the crystal. There are many motifs which impose predictable structures and many functional groups that allow extended hydrogen bond aggregates to form. The presence of symmetry elements in the crystal like the center of symmetry, mirror planes, rotation axes provide nodal points around which hydrogen bonded templates can self propagate in the entire lattice.

For example, a tape motif is formed when a molecule in the structure is hydrogen bonded to two neighboring ones as shown in Fig. 1(a). The hydrogen bond between any two molecules form a cyclic eight-membered ring utilizing the center of symmetry in the lattice. The consequent generation of the unit cell about these centers of symmetry would provide an energy minimized conformation for such molecular assemblies to propagate in all directions [14]. A ribbon motif is generated

when each molecule is hydrogen bonded to two or three molecules, regardless of the connectivity in the hydrogen bonds between the molecules (Fig. 1b,c). The chain motif is an attractive mold for the design of 1-D array of molecules whereas the layer and sheet motifs lead to 2- or 3-D aggregates of molecules. In any event, the presence of symmetry elements provide the loci for the formation of all these various types of motifs, if and whenever present. It is interesting that the formation of these hydrogen bonded networks provide the scaffoldings albeit the symmetry elements. However, there are hardly any examples which do not utilize the symmetry element in the crystal lattice for the construction of the frameworks. It may be mentioned here that this design feature is a setback for the generation of nonlinear optical (NLO) materials via hydrogen bonded networks since the energy minimized networks across symmetry elements are more stable than the ones without. Extensive studies on hydrogen bonding have resulted in the classification of networks in terms of the degrees of translation freedom. Hydrogen bonded  $\alpha$ -networks of secondary amides [92] result in either single molecule chain or as chains of primary amide dimers (Fig. 2). The assembly with two degrees of

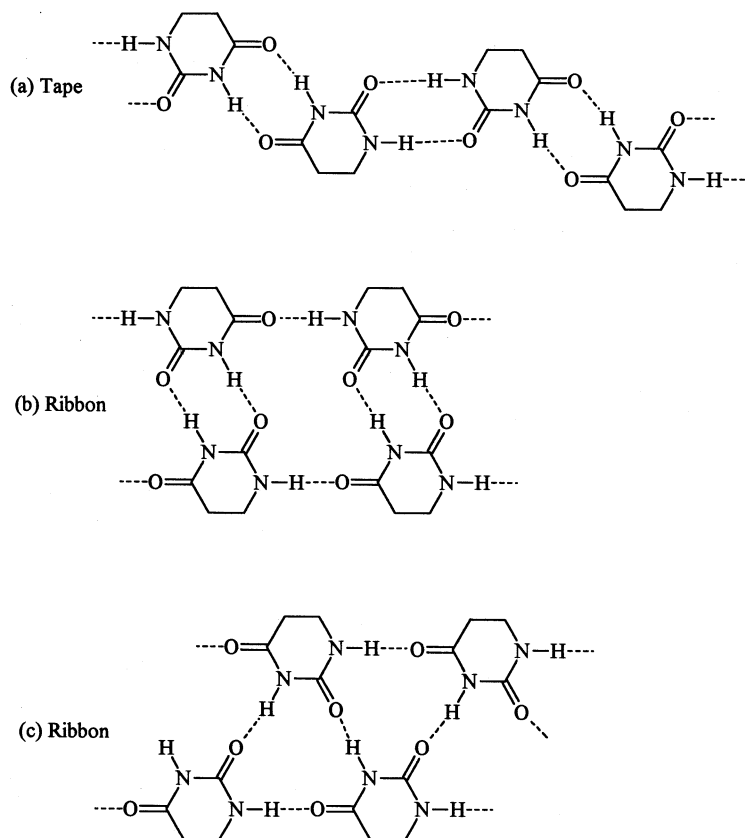


Fig. 1. Hypothetical examples of (a) tape, and (b,c) ribbon motifs formed by amide groups.

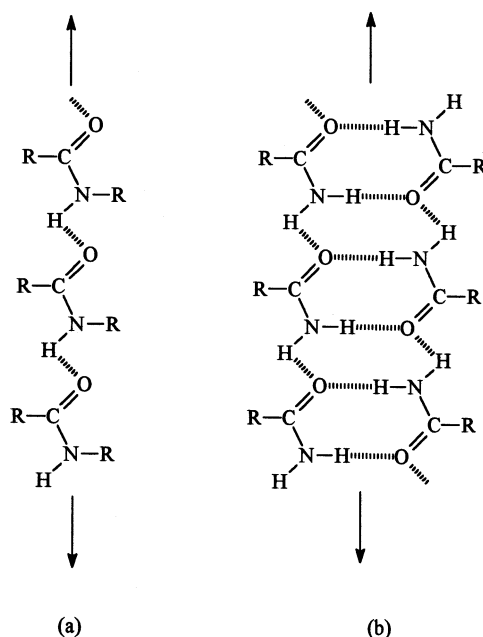


Fig. 2. Examples of  $\alpha$  networks: (i) secondary and (ii) primary amides.

translation symmetry ( $\beta$ -network) is seen in primary diamides [93] (Fig. 3) and generates a layered molecular solid. The  $\gamma$ -network with three degrees of translation freedom generally consists of  $\alpha$ - and  $\beta$ -subnetworks spanning the entire crystal.

### 2.1. The theory of nonlinear optics

The interaction of an electromagnetic field with matter induces a polarization of the electron density around an atom. This displacement of the electron density away from the nucleus generates a charge separation resulting in an induced dipole with moment  $\mu$ . At small field strengths

$$P = \alpha E_o \cos \omega t \quad (1)$$

where  $E_o \cos \omega t$  is the electric field of a plane light wave,  $\alpha$  is the linear polarizability and  $P$  is the polarization.

If the field oscillates with a frequency  $\omega$ , the induced polarization is in phase. The field strength provided by day light [ $10^{-2} \text{ V cm}^{-1}$  (intensity  $< 10 \text{ W cm}^{-2}$ )] will evoke only a linear response. With the advent of lasers with field strengths of the order of  $10^6 \text{ V cm}^{-1}$  (intensity ca.  $10^9 \text{ W cm}^{-2}$ ) a nonlinear response could be observed as the electronic oscillations are now anharmonic. The nonlinear polarization is as follows:

$$P_E = \alpha E_o \cos \omega t + \beta (E_o \cos \omega t)^2 + \gamma (E_o \cos \omega t)^3 + \dots \quad (2)$$

The quantity  $\beta$  is known as the first molecular hyperpolarizability and represents the generation of the second harmonics. If the bulk of the material is considered then:

$$P = P_o + \chi^{(1)}E_o \cos \omega t + \chi^{(2)}E_o^2 \cos(\omega t)^2 + \chi^{(3)}E_o^3 \cos(\omega t)^3 + \dots \quad (3)$$

with  $P_o$  as the static dipole moment of the material and  $\chi^{(n)}$  is the  $n$ th order NLO susceptibility. Eq. (3) can be rewritten as follows:

$$P = (P_o + 0.5\chi^{(2)}E_o^2) + \chi^{(1)}E_o \cos(\omega t) + 0.5\chi^{(2)}E_o^2 \cos(2\omega t) + \dots \quad (4)$$

since  $\cos^2(\omega t) = 0.5 + 0.5 \cos(2\omega t)$ .

Physically, Eq. (4) suggests that the polarization consists of a second order DC field contribution to the static polarization (first term), a frequency component  $\omega$  corresponding to the incident light frequency (second term) and a new frequency doubling component,  $2\omega$  (third term). The generation of twice the input frequency is referred to as the second harmonic generation (SHG).

## 2.2. Materials for second order nonlinear optics

The potential for application in telecommunication, optical data storage and information processing [94–98] make these materials of strategic importance. Though commercially available NLO materials are usually of inorganic origin, organic materials can have several advantages.

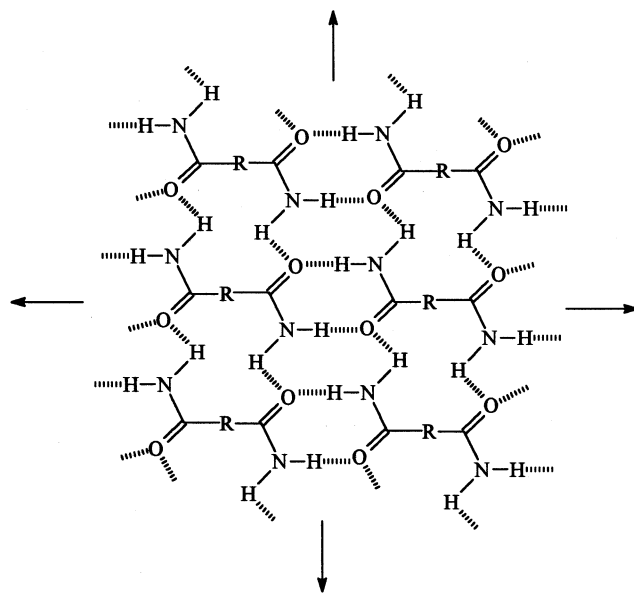


Fig. 3.  $\beta$  network hydrogen bond pattern in primary diamides.

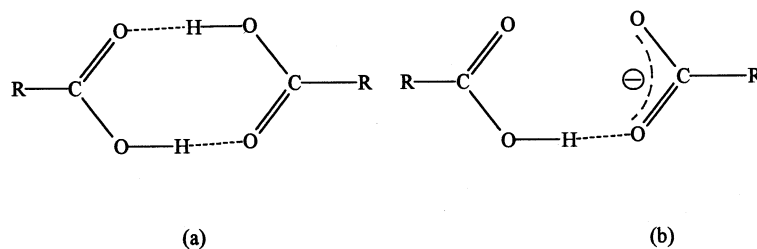


Fig. 4. (a) Dimeric form of a carboxylic acid. (b) Monovalent dicarboxylate anion.

Organic materials are more amenable to structural variations, they possess large second order molecular polarizabilities ( $\beta$ ), more favorable physical properties, higher resistance to optical damage and more versatile for synthetic manipulations. The basic requirements for an organic crystal to exhibit large SHG are as follows:

1. A non-zero nonlinear coefficient.
2. Transparency to the wavelength involved.
3. Efficient transfer of energy between the optical waves propagating through the crystalline material.
4. Good physical and optical properties (large Mohs hardness, low dispersion, etc.).

The major drawback in organic materials has so far been the nonlinearity, transparency trade off [99] and, in many cases, the lack of quality and size of the crystals. Also, nearly 75% of all achiral organic molecule crystallize in centrosymmetric space groups [97]. However, recently there are several examples in literature [100–102] where large sized crystals have been grown using carefully planned crystallization experiments.

Many strategies for forming acentric structures showing SHG have been followed and hydrogen bonded networks [103,104] appear to be the most exciting among all these approaches. The basic necessity is the dipolar alignment favorable for SHG in the crystal lattice.

### 2.3. Hydrogen bonded tartrates as anionic building blocks

Several groups have worked on the approach of combining organic polarizable cations with hydrogen bonding organic anion to produce materials that show SHG activity [105–117]. The anions serve as building blocks leading to structural and thermal stability which ensures selectivity and directionality of the hydrogen bonding pattern. The overall crystal packing is further influenced by the cationic incorporation. Tartaric acid [118] capable of initiating multidirectional hydrogen bonds of stereogenic L-tartaric acid to form acentric crystalline salts with organic bases has generated a family of SHG materials.

The hydrogen bond preferences of carboxylic and dicarboxylic acids are the generation of cyclic head-to-head hydrogen bond motifs in the solid state (Fig. 4a) [119]. Such a network results in a centrosymmetric eight-membered ring with strong

O–H $\cdots$ O bonds resulting in an infinite chain. The symmetry is distorted if one consider the monovalent dicarboxylates thus forming an unhooked chain leading to the annihilation of the possible center of symmetry, as shown in Fig. 4(b). This asymmetric chain formation is the key design feature as the infinite chain formed in the head to tail fashion, generates the scaffolding. The hydroxyl groups are almost at right angles to the infinite chain and are available for cross linking adjacent anionic chains. This generates a 2-D mold and with a counter ion the adjacent layers of anions can be welded to result in a stable, 3-D aggregate. Transforming the hydroxyl groups to O-benzoyl esters would provide additional hydrogen bond acceptor sites. These dibenzoyltartrate networks also provide an additional intra-aromatic stacking forces.

A large number of structures have been solved which involve multidirectional hydrogen bonding in tartrate frameworks and most of these design aspects generate materials suitable for depicting SHG. The crystal packing dictates the orientation of the components in the lattice, and the hydrogen bonded motifs provide a priori predictability of the nonlinear response.

#### *2.4. Conserved frameworks: inclusion of amines and the implications on SHG*

The multidirectional hydrogen bonded tartrate framework provide a conformational rigid environment for the incorporation of cations. A series of anilinium cations with various functional groups as substituents have been used to form salts with L-tartaric acid and D-dibenzoyltartaric acid [113–117]. Most of these salts show second harmonic generation activities comparable to urea (Table 1).

##### *2.4.1. Characteristics of a stable network*

The general features of a stable network are as follows. Each individual component (block) of the network should have the capacity to link to the adjacent block through well directed interactions. These links should be subtle enough to allow for the incorporation of the cations between the strands forming the network. The links must also be strong enough not to allow any delinking during the incorporation. The distance between adjacent strands should allow for cross links between the strands and the cations completing the overall grid pattern of the framework (Fig. 5) [117].

##### *2.4.2. Analysis of frameworks and invariance*

The binary salts of tartrate and dibenzoyltartrate anions provide the characteristics of a stable network and the polarizable cations provide the cross links. The individual tartrate units link to adjacent block through a well directed O–H $\cdots$ O hydrogen bond leading to an intra block (Fig. 5) distance of ca. 2.5 Å. The plot of the back bone torsion angle against the torsion angle involving the oxygen atom at the deprotonated end of the carboxylic ion (Fig. 6) shows that the anions cluster together in the correlation plot. The conformations of the dibenzoyl monohydrogen tartrate units in all the representative salts is also identical and this results in a rigid network regardless of the type of cross-linking cation used. The anionic inter-layer separation is also conserved in all the dibenzoyltartrates (Table 1) and in many tartrate salts. The only variable appears to be the inter-strand separation which depends upon the dimension, shape and nature of the cations. Thus, these anionic framework generate



Table 1  
SHG activity of the salts and the anionic layer separation distance

Entry	Acid	Base	SHG <sup>a</sup>	Layer separation (Å)
1	D-Dibenzoyltartaric acid	2,3-Xylidine	0.79	10.26, 10.46
2	D-Dibenzoyltartaric acid	2,6-Xylidine	0.86	9.62, 9.72
3	D-Dibenzoyltartaric acid	3-Toluidine <sup>b</sup>	0.91	10.15, 10.34
4	D-Dibenzoyltartaric acid	1,4-Diaminobutane	Faint <sup>d</sup>	— <sup>f</sup>
5	D-Dibenzoyltartaric acid	3-Toluidine <sup>c</sup>	0.88	— <sup>f</sup>
6	D-Dibenzoyltartaric acid	2-Toluidine	Nil <sup>e</sup>	9.44
7	D-Dibenzoyltartaric acid	3-Fluoroaniline	Faint <sup>d</sup>	10.34, 10.38
8	D-Dibenzoyltartaric acid	1-Nonylamine	Faint <sup>d</sup>	10.28
9	D-Dibenzoyltartaric acid	1-Decylamine	Faint <sup>d</sup>	10.43
10	L-Tartaric acid	4-Toluidine	1.2	10.97
11	L-Tartaric acid	2-Anisidine	Nil <sup>e</sup>	10.19
12	L-Tartaric acid	2,6-Xylidine	0.82	10.77
13	L-Tartaric acid	3-Bromoaniline	Faint <sup>d</sup>	10.37, 10.77
14	L-Tartaric acid		0.56	
15	D-Dibenzoyltartaric acid		1.00	
16	N,N'-Bibenzyl-L-tartramide		0.89	

<sup>a</sup> All SHG intensities measured with respect to urea.

<sup>b</sup> Stoichiometric variant 1:1.

<sup>c</sup> Stoichiometric variant 1:2.

<sup>d</sup> SHG activity around that of quartz.

<sup>e</sup> No detectable SHG activity.

<sup>f</sup> Absence of infinite anionic network.

pre-fabricated inflexible matrices for the incorporation of the cations. It is remarkable to notice that the SHG in all these cases does not exceed the value of the spacer units (L-tartaric acid, D-benzoyltartaric acid) which build the framework. In a recent report [117], we have classified these salts into three categories, Type I, in which the

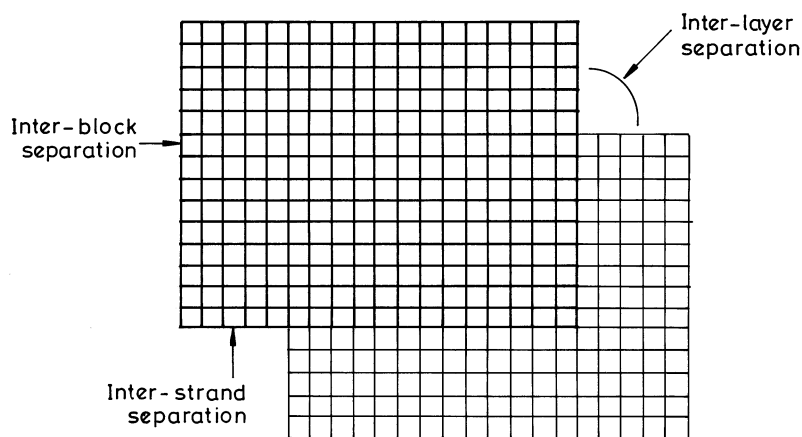


Fig. 5. A representative view of the overall grid pattern in a H-bonded framework.

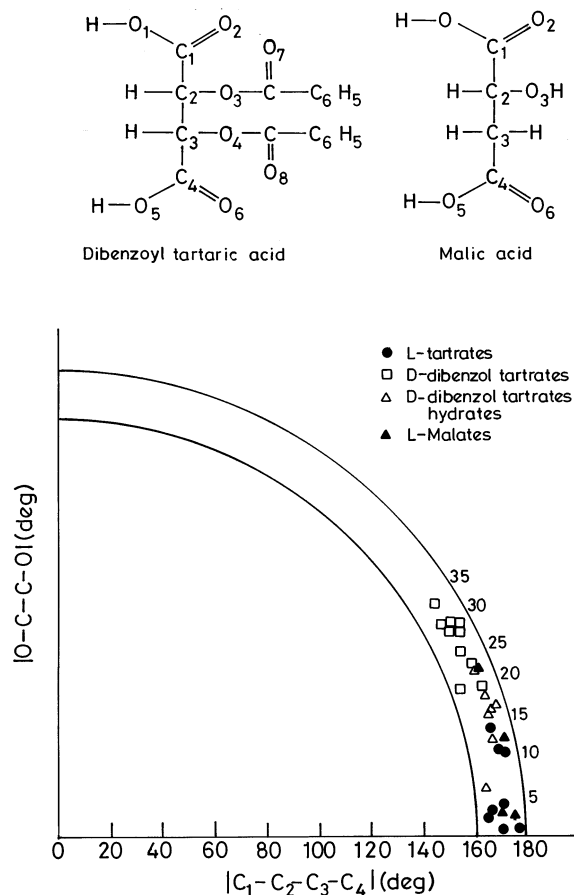


Fig. 6. The polar plot of back bone torsion angle versus torsion angle involving oxygen atom at the deprotonated end of the carboxylic ion.

framework structures are conformationally rigid, Type II, in which the infinite chain motifs are no longer parallel to each and the inter-layer separation is not intersected with crisscross hydrogen bonding and hence not conserved like in the case of 2-amino-5-nitropyridinetartrate [57]. The value of SHG in such cases is much higher than that of urea (3.2 times). The presence of solvent molecules also generally deter the formation of hydrogen bonded motifs and hence there is no well defined inter-layer separation. Interestingly, the packing modes are recast (Fig. 7) and the space between the chains appear to widen as additional inter chain hydrogen bonds get formed including the solvent molecule [116]. These structures fall into the Type III category.

An analysis of the torsion angle between the chains and the inter-layer separation (Table 2) clearly shows the restraints between these layers. The Type I cases, which corresponds to the conserved inter-layer separation of (ca. 10 Å), show SHG restrained to that of the spacer units. The fact that the value of SHG is restricted

to that of the framework provides directives towards the design aspects of futuristic materials. The cation incorporation invariably should possess hydrogen bonding features which do not allow the conservation of inter-layer separation distance (Type II class). It is also suggest that selective structural alterations could be done on the rigid framework to enhance its own SHG. Alternately, other monocovalent interactions other than hydrogen bonding may be explained for the effective maximization of SHG in materials. Solvent molecule incorporation in the scaffoldings also appear to deter the depiction of SHG.

### 3. Fluorine as a design element in solid state photochemistry

Schmidt and co-workers [120–122] discovered the correlation between the reactive molecular arrangement in crystals and the configuration of the photoproduct which results upon irradiation. The photoproducts are classified as  $\alpha$ ,  $\beta$ , and  $\gamma$  based on the geometrical disposition of the individual monomers. The  $\alpha$ -modification has centrosymmetric related double bonds and yields a centrosymmetric dimer on irradiation. The  $\beta$  modification has reactive double bonds related by translation symmetry and upon irradiation gives a photoproduct with a mirror plane. In both

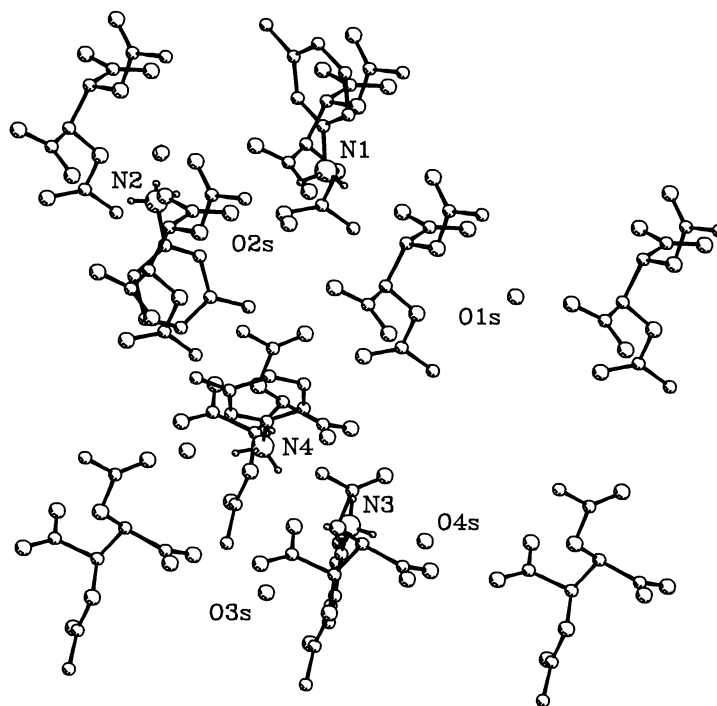


Fig. 7. Hydrogen bonding features in the structure of 3-toluidinium-D-dibenzoyltartrate dihydrate (1:2), indicating that the incorporation of solvent water leads to modified packing modes.

Table 2

Torsion angle between adjacent chains and the type classification

Structure	Torsion angle $\theta$ (°)	Classification type
<i>Tartaric acid with</i>		
<i>m</i> -Anisidine	0.0	I
<i>p</i> -Toluidine	2.96	I
2,6-Xyldine	4.56	I
Bromoaniline	0.0	I
Guanidine	130.5	II
Phenylethylamonia	−42.18	II
Bis-piperazine	−106.48	II
Imidazole	9.11	I
Benzimidazole	0.0	I
2-Amino-5-nitropyridine	117.43	II
<i>Dibenzoyltartrate with</i>		
2,3-Xyldine	2.29	I
2,6-Xyldine	4.86	I
3-Toludine	7.18	I
2-Toludine	5.80	I
3-Fluroaniline	0.08	I
Nonylamine	0.87	I
Decylamine	8.58	I

cases the distance between the reactive double bonds is generally  $< 4.2$  Å. In the  $\gamma$ -form there is no reaction and the reactant molecules have their double bonds separated by  $> 4.2$  Å. One of the key offshoots of such observation is the design of tools in crystal engineering to ensure the pre-organization of the reactant molecules for dimerization or otherwise. The overall 3-D packing in the crystal lattice is generally the key feature which controls weak but well directed interactions between molecules involving hydrogen bonds, halogen–halogen interactions, stacking interactions, etc. Extensive studies have demonstrated the ability of chloro, bromo, methoxy and acetoxy groups to steer reactant molecule in the lattice for photodimerization [31,123–126].

### 3.1. Fluoro substituted styrylcoumarins

Fluorine is by far the least studied, even though in a planar molecule like coumarin, fluoro substitution leads to  $\beta$  packing mode [71]. In non-planar benzyldene-DL-piperitone, the  $\alpha$  packing mode is observed. The photo behavior in substituted or unsubstituted styrylcoumarins generally yield *anti*-HT centrosymmetric dimers upon irradiation. The manner in which a covalently bound fluorine acts to steer molecules to close proximity is an activity currently pursued. The van der Waal radius of fluorine (1.47 Å) lies between that of hydrogen (1.20 Å) and oxygen (1.52 Å). Based on only atomic size, fluorine does not seem to be very different from hydrogen. The crystal structures of chlorine, bromine and iodine have

halogen–halogen short contacts less than the sum of the van der Waal's radii whereas no such contacts are observed in the crystal structures with fluorine. It appears as though the covalently bound fluorine is unable to formulate intermolecular interactions due to its low proton affinity. Based on the analysis of C–F bond interactions with hydrogen bond donors, it has been recently demonstrated that fluorine rarely accepts hydrogen bonds [81].

A systematic crystallographic investigations of several fluoro substituted styrylcoumarin have indicated the preference for the  $\beta$  packing modes (*syn* HH) is marginal and indeed out of the ten crystal structures studied so far six possess  $\beta$  packing modes (Fig. 8) [78]. These six structures pack in a manner which ensures one of the crystallographic axes is  $< 4.2$  Å. The observed densities in these crystals generally are higher than the corresponding unsubstituted styrylcoumarins demonstrating that fluorine has a dominant role in steering these molecules into  $\beta$  packing modes. A consequent dramatic effect is seen in the length of one of the cell dimensions being very large (ca. 30–60 Å). This further ensures that most of these crystals grow as needles. Remarkably there are no C–H $\cdots$ F interactions.

The crystal structures of compounds 4-(3-fluorostyryl)coumarin, 4-styryl-6-fluorocoumarin and 4-styryl-7-fluorocoumarin have the molecular aggregates in an  $\alpha$  packing mode [79]. These crystallize with no unusually large cell dimension and have possible C–H $\cdots$ F interactions. The molecular arrangements also show a possible C=O $\cdots\pi$  interaction between the centrosymmetrically-reactive partners (Fig. 9) [127]. Interestingly, the cell dimensions appear very normal and there is no unusual lengthening of an axis in these  $\alpha$  packed structures.

### 3.2. Fluoro substituted butadienes

In all styrylcoumarins there are two reactive double bonds—the pyrone and the styrenic. In principle both could undergo photodimerization but so far in literature all derivatives except one [128] react across the styrenic bond. There is no case of photodimerization occurring at both double bonds unlike in molecules with multiple reactive double bonds [129,130]. Photo behavior of diolefinic compounds, (1*E*,3*E*)-1-pentafluorophenyl-4-(4-methoxyphenyl)-1,3-butadiene, (1*E*,3*E*)-1-pentafluorophenyl-4-(4-methylphenyl)-1,3-butadiene and (1*E*,3*E*)-1-pentafluorophenyl-

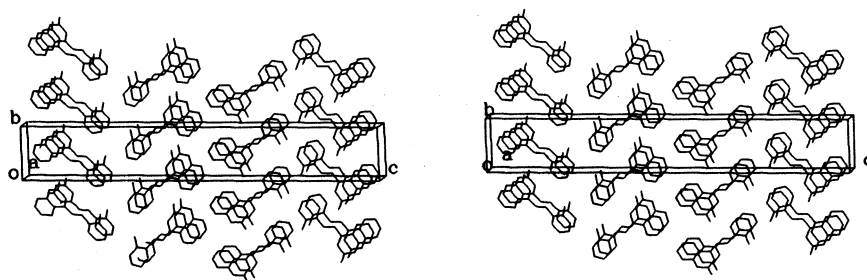


Fig. 8. A representative stereo packing diagram of  $\beta$ -packed fluoro-substituted styrylcoumarin.

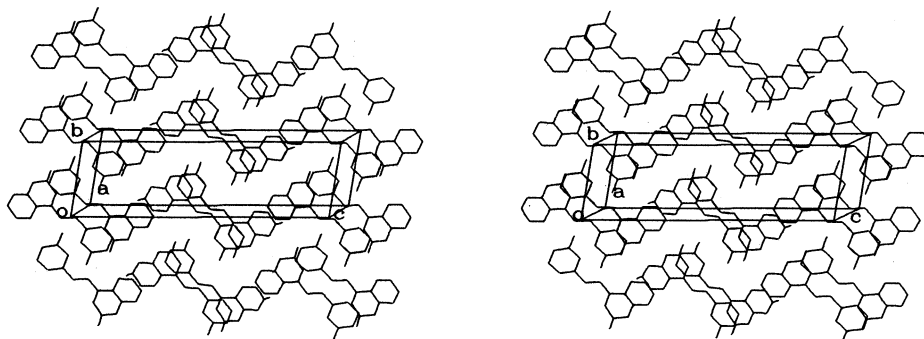


Fig. 9. A representative stereo packing diagram of  $\alpha$ -packed fluoro-substituted styrylcoumarin.

4-phenyl-1,3-butadiene yield a single double photo dimer (*anti*-HT  $\alpha$ -packing mode) (Fig. 10). Based on the percentage yield of the products it has been predicted that the reaction might occur in a step wise fashion one double bond at a time. Even with five fluorine atoms on the phenyl ring there are very few F...F short contacts.

#### 4. Polymorphic modifications: coumarin as an agent

In a major lead article [131] the role of tailor-made auxiliaries for the control of nucleation and growth of molecular crystals was discussed. Generation of crystals of different morphologies [132] as also crystals with different molecular organization in the lattice by the addition of small amounts of another material with shape similarity [131] provides an additional tool in engineering molecules in preferred orientations. Coumarin, qualifies as an orienter of this type and could be employed for generating polymorphic modifications in styrylcoumarins [133].

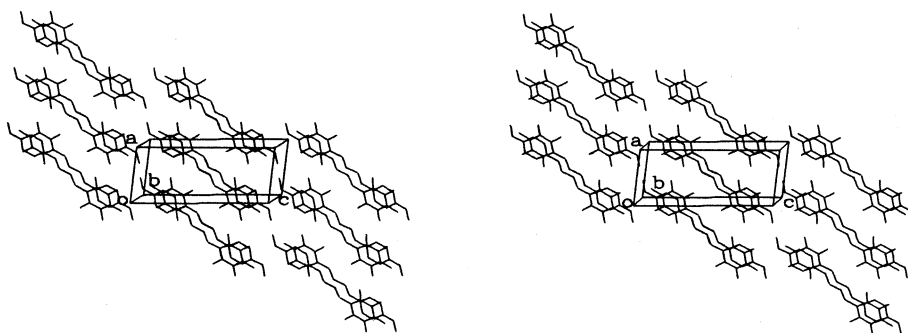


Fig. 10. Stereo packing diagram showing the molecules which are ready for double-photo dimerization.

Table 3

Crystallographic details of the polymorphic modifications in styrylcoumarin

Morphology	Plates/on coumarin addition	Prisms	Needles
Molecular formula	$C_{17}H_{12}O_2$	$C_{17}H_{12}O_2$	$C_{17}H_{12}O_2$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
$a$ (Å)	17.057(3)	11.082(2)	13.418(4)
$b$ (Å)	8.229(3)	11.215(3)	5.720(4)
$c$ (Å)	18.261(3)	12.127(3)	17.840(3)
$\alpha$ (°)	90.00	102.35(2)	90.00
$\beta$ (°)	96.33(2)	116.41(2)	110.79(2)
$\gamma$ (°)	90.00	98.62(2)	90.00
$Z$	8	4	4
$V$ (Å <sup>3</sup> )	2569.2(11)	1265.9(6)	1280.1(10)
$D_{\text{calc.}}$ (mg m <sup>-3</sup> )	1.295	1.303	1.288

4-Styrylcoumarin crystallizes from a mixture of chloroform and hexane in a 1:1 ratio, resulting in two polymorphs (needles and prisms) which can be separated under a microscope. The crystal structures of these two have been established unequivocally [128]. To the crystallization vessel of 4-styrylcoumarin, coumarin was added in small amounts (2.5% by molar ratio) and the new morphology of the resulting crystals were plates and the detailed crystal structure analysis clearly established that the molecules of 4-styrylcoumarin now are arranged in a totally new crystal lattice and there is no trace of coumarin (Table 3) [133]. The distribution of the residual electron density ( $\pm 0.09 \text{ e } \text{\AA}^{-3}$ ) does not correspond to any coumarin connectivity. The powder diffraction pattern obtained on a sample of crushed and finely ground crystals also supported this argument (Fig. 11). Addition of excess of coumarin does not alter the crystal habit and the excess coumarin either precipitates out or remains in the mother liquor.

Crystals of 4-(3-fluorostyryl)coumarin grow as needles (space group  $P\bar{1}$ ) and the molecular assembly is suitable for the generation of the centric H–T dimer. Addition of coumarin (again 2.5% molar ratio) does not seem to alter the crystal habit as (needles) but X-ray crystallography shows that the crystals are now in the space group  $Pc$  (Table 4) with the molecular assembly in the lattice suggesting in favor of a mirror (*syn*-H–H) dimer [133]. The formation of such a *syn*-H–H dimer was confirmed upon irradiation by spectroscopic studies.

Addition of coumarin seems also to produce X-ray quality crystals in case of *trans,trans*-1,4-diphenyl-1,3-butadiene [133]. Thus addition of a shape-selective moiety to realize polymorphic modifications in the crystalline lattice and hence on the supramolecular assemblies appears to emerge as a major tool in the design and fabrication of materials with tailor-made properties.

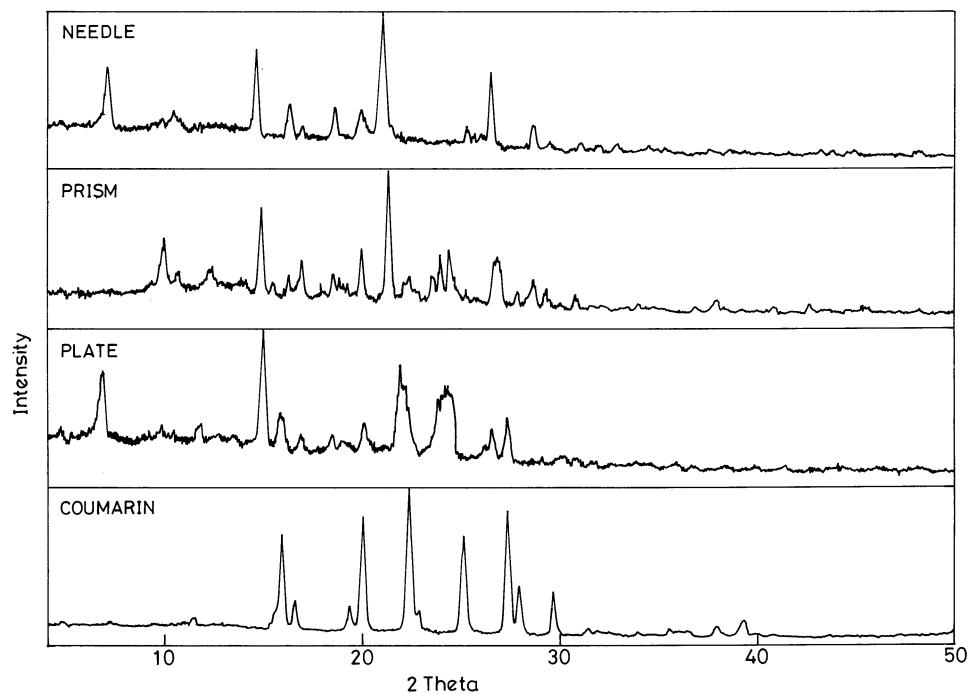


Fig. 11. X-ray powder diffraction patterns showing the formation of a new polymorph of styrylcoumarin—plates (as compared to needles, prisms and coumarin alone).

## 5. Conclusions

Based on the results outlined above the use of multi-faceted hydrogen bonding substitution of organic fluorine and coumarin as an additive serve as design

Table 4  
Crystallographic details of 3-fluorostyrylcoumarin

Morphology needles	After coumarin addition	Before coumarin addition
Molecular formula	$C_{17}H_{11}FO_2$	$C_{17}H_{11}FO_2$
Crystal system	Monoclinic	Triclinic
Space group	$Pc$	$P\bar{1}$
$a$ (Å)	6.879(3)	7.358(1)
$b$ (Å)	3.929(1)	7.652(1)
$c$ (Å)	23.459(9)	23.829(3)
$\alpha$ (°)	90.00	97.04(1)
$\beta$ (°)	90.35(4)	96.03(1)
$\gamma$ (°)	90.00	101.78(1)
$Z$	2	4
$V$ (Å <sup>3</sup> )	634.0(4)	1291.8(3)
$D_{calc.}$ (mg m <sup>-3</sup> )	1.395	1.369



elements for the generation of tailor-made materials. The analysis of hydrogen bonded tartrate amine complexes in terms of packing modes, interactions resulting in well organized rigid frame works, cationic orientations and the subsequent implications on SHG provide pointers to the design of materials for second harmonic generation in future. The behavior of fluorine, though intriguing, and the consequent reorganization in supramolecular assemblies bring out the features of both size and charge characteristics relevant in the design of photodimers of coumarin related molecules. The lack of intermolecular interactions involving fluorine clearly suggests that the organic fluorine prefers a C–F over C=F even though fluorine is most electronegative element in an aromatic framework. The generation of polymorphic modifications on adding shape similarity additives is expected to emerge as a dominant factor in crystal engineering and its applications are bound to have an impact in the construction of materials with preconceived properties. This design element is also expected to find an immediate application in drug design.

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