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PAPER

Solid state photodimerization of *trans*-2-(4-pyridyl)-4-vinylbenzoic acid *via* salt formation and isomerisation of cyclobutane compounds in solution†

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Several salts of *trans*-2-(4-pyridyl)-4-vinylbenzoic acid (HPVBA) obtained by reacting with inorganic acids and organic diamines are discussed in the context of their solid state packing and photoreactivity. The acids CF₃CO₂H, HClO₄, HNO₃, H₂SO₄ produced salts where H₂PVBA⁺ cations are oriented parallel in *head-to-tail* (HT) fashion, however, the trifluoroacetate salt did not undergo photodimerization. The *head-to-tail* (HT) parallel orientation was inversed to *head-to-head* (HH) orientation by incorporating excess H₂SO₄ during salt formation. Thus two stereoisomers *viz.* HT- and HH-dimers were obtained from salts derived from same salt-former. Salts were also made exploiting carboxylic acid functionality by employing ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane and it was found that only the salt obtained with 1,4-diaminobutane undergo photodimerization. In an analogy, it is shown that in spite of poor predictability, the strategy of salt formation works well and has significant impact in the synthesis of functional cyclobutane derivatives.

Introduction

Research on combining two photoreactive C=C bonds into a cyclobutane ring has become a focused area in crystal engineering, organic photochemistry and solid state chemistry.¹ Although there are some exceptions, it is an accepted fact that the photodimerization reaction happens between two C=C bonds aligned parallel and separated within 4.2 Å (Schmidt's criteria).² The contact geometry of two reacting bonds is crucial for the formation of the right isomer of the product. The understanding of crystal engineering principles and their proper utilizations have resulted in parallel arrangements of C=C bonds suitable for photodimerization reaction. In this regard, several co-crystals,³ organic salts,⁴ discrete⁵ and polymeric⁶ coordination compounds have extensively been studied. Another important aspect of studying these systems, apart from their solid state packing, is accessing novel cyclobutane compounds with specific geometry and desired functional groups which can be utilized as potential ligands for making metal–organic materials.^{4g,7}

Among the hydrogen-bonded co-crystals studied so far, resorcinol is the mostly employed template for aligning C=C bonds of olefin containing pyridyl groups.^{3a–f} The C=C bonds of certain dicarboxylic acids have also been aligned parallel using template containing pyridyl groups and *vice versa*.^{3g–i} Other than

trans-cinnamic acid and related compounds, mainly symmetric olefin compounds have been engineered in the crystalline state. However, unsymmetric olefins are rather more interesting and challenging where two possible orientations *viz.* *head-to-head* (HH) and *head-to-tail* (HT) can be controlled by applying crystal engineering principles.^{4h,4j,8} Recently, MacGillivray *et al.* have reported that two unsymmetric olefins namely *trans*-3-(4'-pyridyl) acrylic acid (4-PA) and HPVBA were difficult to co-crystallize with resorcinol-derived templates due to synthon competition in the presence of carboxylic acid groups, a competitor of phenols for hydrogen bonding with pyridyl groups.⁹ In addition, only HH-dimer of an unsymmetric olefin can be obtained from co-crystals using resorcinol-type templates. In our early contribution, we have reported the strategy of salt formation at pyridyl site with strong inorganic acids for the synthesis of both HH- and HT-dimers of 4-PA.^{4h,4j} The parallel orientation of pyridyl cations in HT-fashion is stable due to cation– π interaction,^{4d–f,10} whereas, the HH-arrangement is quite unstable due to cation–cation repulsion which could be stabilised by the presence sulphate bi-anion. Unsymmetrical pyridyl carboxylic acids like 4-PA and HPVBA have another advantage of forming salts with strong amines, in addition to with inorganic acids, utilizing their carboxylic acid functionality.

In this study, we have extrapolated the strategy of salt formation with HPVBA, a relatively longer olefin has been chosen to allocate hetero-functionality to the cyclobutane ring, in order to obtain both the HH- and HT-dimer *via* photodimerization reaction of its salts. We have exploited both the pyridyl and carboxylic acid functionality to make its salts with strong inorganic acids as well as with organic amines, respectively.

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Results and discussion

HPVBA was allowed to react with various strong acids and amines. All the molecular salts were synthesized from aqueous media and the diffraction quality single crystals were grown by slowly evaporating their alcoholic solutions.† The yields of these crystallization processes vary in the ranges of 90–95%.

Trifluoroacetate salt of HPVBA (1)

The single crystals of anhydrous salt of composition $(\text{H}_2\text{PVBA})(\text{CF}_3\text{CO}_2)$ (**1**) were grown by evaporating methanolic solution slowly and the structure was refined in triclinic space group, $P\bar{1}$. As expected, the pyridyl group of HPVBA was found to be protonated. Various kinds of charge assisted hydrogen bonding like $\text{N-H}\cdots\text{O}$, $\text{O-H}\cdots\text{O}$, $\text{C-H}\cdots\text{O}$ play important roles to construct the solid-state structure as shown in Fig. 1. One oxygen atom of the TFA anions form $\text{N-H}\cdots\text{O}$ hydrogen bonds to a H_2PVBA^+ cation and another oxygen form $\text{O-H}\cdots\text{O}$ hydrogen bonds to carboxylic acid group of another H_2PVBA^+ cation and therefore, clipping them in parallel orientation in a *head-to-tail* fashion (Fig. 2). The distance between the $\text{C}=\text{C}$ bonds is found to be 4.235 Å and the salt was found photostable under UV light although the distance is almost at the borderline of Schmidt's distance criteria.²

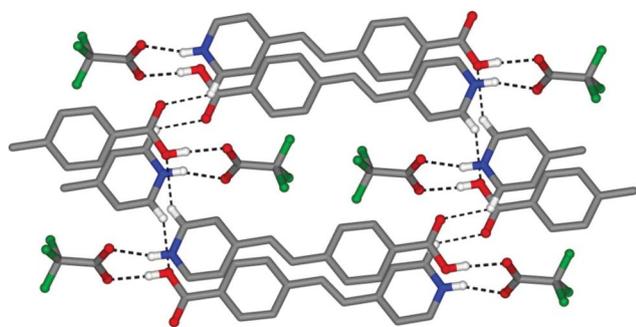


Fig. 1 Various kinds of supramolecular interactions in **1**.

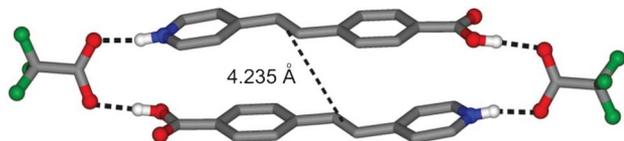


Fig. 2 The *head-to-tail* parallel orientation of H_2PVBA^+ clipped by TFA anions. The C-H hydrogen atoms are omitted.

† Crystal data for **1** at 100(2) K: $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NO}_4$, $M = 339.27$, triclinic, space group $P\bar{1}$, $a = 7.2580(9)$, $b = 8.4271(10)$, $c = 12.6094(15)$ Å, $\alpha = 77.860(2)^\circ$, $\beta = 75.529(2)^\circ$, $\gamma = 72.829(3)^\circ$, $V = 705.67(15)$ Å³, $Z = 2$, $D_c = 1.597$ g cm⁻³, $\mu = 0.140$ mm⁻¹, Goof on $F^2 = 1.091$, final $R_1 = 0.0578$, $wR_2 = 0.1395$ [for 2895 data $I > 2\sigma(I)$]. Crystal data for **2** at 223(2) K: $\text{C}_{15}\text{H}_{16}\text{ClNO}_7$, $M = 357.74$, triclinic, space group $P\bar{1}$, $a = 8.6037(11)$, $b = 9.5432(12)$, $c = 10.2702(13)$ Å, $\alpha = 93.248(2)^\circ$, $\beta = 101.615(2)^\circ$, $\gamma = 107.129(2)^\circ$, $V = 783.27(17)$ Å³, $Z = 2$, $D_c = 1.517$ g cm⁻³, $\mu = 0.283$ mm⁻¹, Goof on $F^2 = 1.221$, final $R_1 = 0.0784$, $wR_2 = 0.2203$ [for 3008 data $I > 2\sigma(I)$]. Crystal data for **4** at 223(2) K: $\text{C}_{56}\text{H}_{52}\text{N}_4\text{O}_{21}\text{S}_3$, $M = 1213.20$, triclinic, space group $P\bar{1}$, $a = 11.1151(9)$, $b = 11.8964(9)$, $c = 22.1546(18)$ Å, $\alpha = 91.414(2)^\circ$, $\beta = 98.911(2)^\circ$, $\gamma = 110.246(2)^\circ$, $V = 2705.6(4)$ Å³, $Z = 2$, $D_c = 1.489$ g cm⁻³, $\mu = 0.224$, mm⁻¹, Goof on $F^2 = 1.035$, final $R_1 = 0.0652$, $wR_2 = 0.1352$ [for 8465 data $I > 2\sigma(I)$]. Crystal data for **8** at 100(2) K: $\text{C}_{40.75}\text{H}_{39}\text{N}_4\text{O}_{6.75}$, $M = 692.76$, monoclinic, space group $P2_1/n$, $a = 10.1643(11)$, $b = 10.1819(10)$, $c = 34.305(4)$ Å, $\beta = 95.067(3)^\circ$, $V = 3536.4(6)$ Å³, $Z = 4$, $D_c = 1.301$ g cm⁻³, $\mu = 0.089$ mm⁻¹, Goof on $F^2 = 1.072$, final $R_1 = 0.0861$, $wR_2 = 0.2053$ [for 3999 data $I > 2\sigma(I)$].

Perchlorate salt of HPVBA (2)

Single crystal X-ray analysis revealed that the salt of composition $(\text{H}_2\text{PVBA})\text{ClO}_4 \cdot \text{MeOH}$ (**2**) crystallizes in the triclinic space group, $P\bar{1}$. Various types of hydrogen bonding interactions including $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$, $\text{C-H}\cdots\text{O}$ play crucial roles to construct the solid state structure. The pyridinium cations form charge assisted hydrogen bonding with one ClO_4^- anion in $R_2^2(7)$ fashion and interact with another ClO_4^- ion in $C(2)$ fashion *via* weak $\text{C}(\alpha)\text{-H}$ bonds.¹¹ The carboxylic acid groups are involved in hydrogen bonding with methanol molecules, in $R_4^4(12)$ fashion to form a carboxylic acid dimer synthon (*via* methanol). A thorough perusal of the crystal structure reveals that the H_2PVBA^+ cations are aligned parallel in *head-to-tail* fashion with a distance of 3.837 Å between two $\text{C}=\text{C}$ bonds (Fig. 3). Upon irradiation under UV light for 40 h, the single crystals of this salt were found to furnish only 80% photodimerization as monitored by ¹H NMR spectroscopy from the appearance of a multiplet peak for cyclobutane protons to δ 5.01 ppm. The incomplete conversion might be due to the change in the crystal structure accompanied by the loss of MeOH solvent molecules in the process of dimerization. When the salt of the dimer compound was neutralised with aqueous NaOH, the peak for cyclobutane protons shifts at δ 4.69 (m) ppm but two doublet of doublet peaks were not observed as they have been generally observed for *rectt*-HT-4,4-BPCD.^{4h,4j} This may be due to the fact that the cyclobutane protons with 4-pyridyl and 4-carboxyphenyl substituent are almost degenerate (see ESI†). The photoreaction of this salt can be employed to synthesize a new cyclobutane derived ligand *viz.* *rectt*-1,3-bis(4'-carboxyphenyl)-2,4-bis(4''-pyridyl)cyclobutane or *rectt*-HT-4,4-BCBPCB.

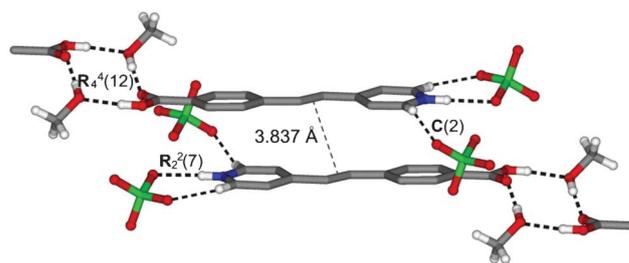


Fig. 3 The *head-to-tail* parallel arrangement of H_2PVBA^+ cations in **2**. The C-H hydrogen atoms are omitted.

Another interesting point to note is that methanol molecules present in the structure have a significant role in the packing of H_2PVBA^+ cations. The same salt when crystallized from ethanol and 1,4-dioxane separately were both found not to undergo any photodimerization. The single crystal obtained from ethanol was too small for the intensity data collection. The rapid loss of 1,4-dioxane from single crystals when taken out of the mother liquor also prevented us from determining its structure. However, both of their compositions were determined by elemental analysis and TGA to be $(\text{H}_2\text{PVBA})\text{ClO}_4$ (**3**) (as 1,4-dioxane is lost from the system). The photostability of this anhydrous salt (obtained from ethanol) and the photoreactivity of the solvated salt (containing methanol) clearly indicate that methanol played some template effect during crystallization which led to the parallel arrangement of H_2PVBA^+ cations. Therefore, the partial

conversion (80%) can be accounted to the loss of MeOH solvent from the single crystals during the process of photodimerization.

Sulphate–bisulphate salt of HPVBA (4)

HPVBA was also reacted with H_2SO_4 in methanol and the single crystals obtained were tested for their photoreactivity. The hydrated salt of composition $(\text{H}_2\text{PVBA})_4(\text{HSO}_4)_2(\text{SO}_4)\cdot\text{H}_2\text{O}$ (**4**) crystallizes in the triclinic space group, $P\bar{1}$. The asymmetric unit contains one formula unit namely, four H_2PVBA^+ cations, two bisulphate anion, one sulphate anion and one water molecule. As expected, various types of neutral and charge assisted hydrogen bonding like $\text{N}\cdots\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}\cdots\text{O}$ are present in the solid-state structure as shown in Fig. 4. The carboxylic acid groups of H_2PVBA^+ cations form carboxylic acid dimer homosynthon ($\text{R}_2^2(8)$). The water molecule present in this salt also donates hydrogen bonding to sulphate and bisulphate anions and accepts from the protonated pyridyl group ($\text{H}\text{--}\text{N}$) of H_2PVBA^+ cation and forms an H-bonded ring with graph set $\text{R}_6^4(16)$. The $\text{C}(\alpha)\text{--}\text{H}$ of H_2PVBA^+ cations also interact with the neighbouring sulphate/bisulphate anions but are not shown in the Fig. 4 for clarity.

Now if we look at the relative orientations of H_2PVBA^+ cations, the combination of both the *head-to-head* and *head-to-tail* manner are observed. All four H_2PVBA^+ cations in the asymmetric unit, labelled as **A–D** in Fig. 4, are oriented in HH-fashion with distances between $\text{C}=\text{C}$ bonds of 4.617, 4.772 and 5.304 Å. All these distances are not favourable for photodimerization reaction. However, when we analyze the relative orientations of H_2PVBA^+ units which are related by a centre of inversion, we see that they (**A** and the one below in Fig. 4) are orientated parallel in an HT-fashion. The distance between $\text{C}=\text{C}$ bonds is 3.772 Å, which is well within the range of Schmidt criteria. Therefore, among the four H_2PVBA^+ cations in the asymmetric unit one is expected to be photoreactive and the compound is supposed to show 25% photodimerization reaction in HT-fashion. When this compound was irradiated under UV

light for 50 h, we observed only about 25% photodimerization in ^1H NMR spectroscopy leading to the formation of HT-BCBPCB (Fig. 5).

When HPVBA was reacted with an excess of H_2SO_4 in water, an intense yellow coloured solid was obtained (**5**). Surprisingly, this yellow solid furnished 80% photodimerization in *head-to-head* fashion upon irradiation under UV light for 50 h, which was confirmed by ^1H NMR spectroscopy (Fig. 5). The formation of HH-dimer 1,2-bis(4'-carboxyphenyl)-3,4-bis(4''-pyridyl)cyclobutane or *rectt*-HH-4,4-BCBPCB was confirmed by the presence of two doublet peaks at δ 4.93 and 4.83 ppm, which can be correlated with the ^1H NMR spectrum of *rectt*-HH-4,4-BPCD discussed in our previous papers.^{4h,4j} When this UV irradiated product was neutralised with NaOH (aq.), these two doublet peaks coalesce to a single doublet peak at δ 4.68 ppm. The composition of this precipitated yellow powder was determined by TGA and elemental analysis to be $(\text{H}_2\text{PVBA})_3(\text{HSO}_4)_3(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_{6.5}$ (see experimental section for details†). Therefore, the amount of H_2SO_4 added during salt formation is very crucial and led to a different packing of H_2PVBA^+ cations and entirely opposite photoreactivity. The role of extra H_2SO_4 in the packing of H_2PVBA^+ cations is not clearly understood due to the lack of a single crystal structure. To the best of our knowledge this type of control over the orientation of the $\text{C}=\text{C}$ bonds and the resultant stereochemistry of the products in photodimerization reaction just by changing the composition of the salt was not known before.

Photoreactivity of salts of HPVBA with HNO_3 and HCl

HPVBA was also reacted with HNO_3 and HCl and the resulting yellow crystalline samples were studied for their photoreactivity. We could not grow diffraction quality single crystals for both but the composition of these salts were determined by elemental analysis and TGA. An anhydrous salt of composition $(\text{H}_2\text{PVBA})\text{NO}_3$ (**6**) was synthesized with HNO_3 , which underwent quantitative photodimerization upon irradiation under UV

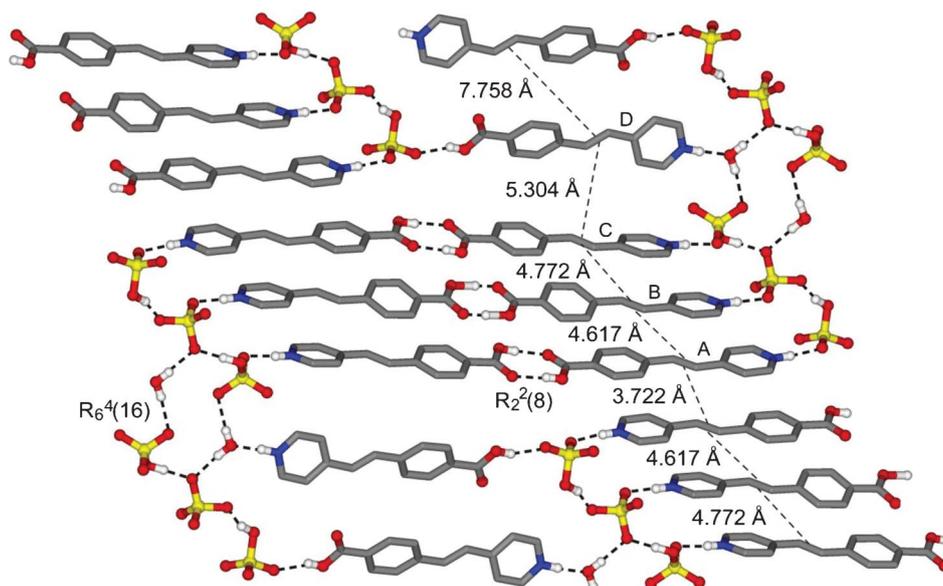


Fig. 4 The crystal structure of sulphate–bisulphate salt of HPVBA, **4**. The C–H hydrogen atoms are omitted.

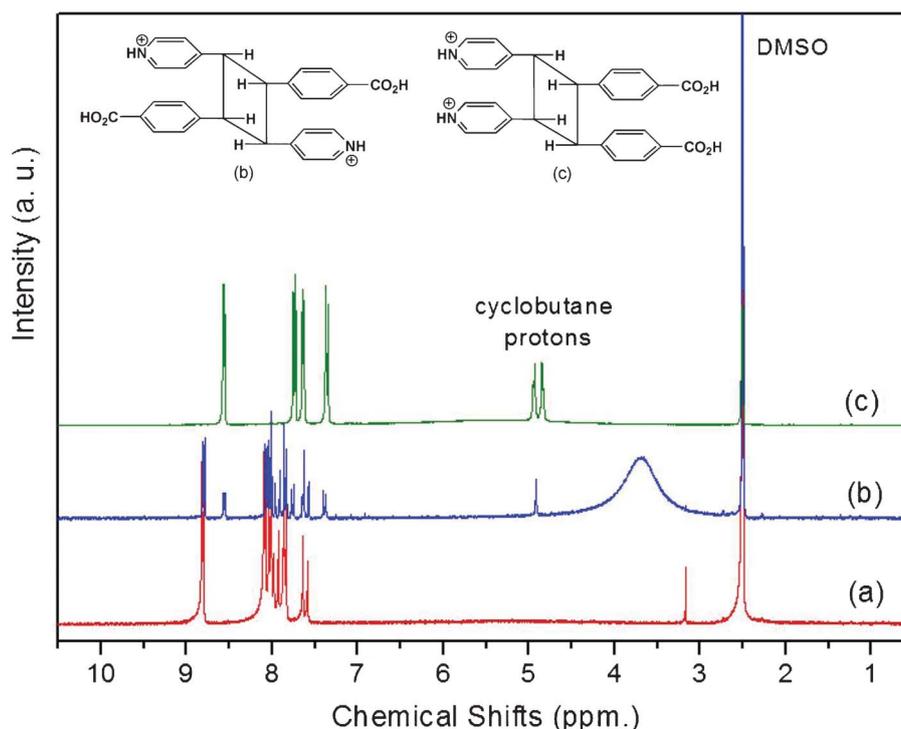


Fig. 5 ^1H NMR spectra of **4** before (a) and after (b) UV irradiation; (c) for **5** after UV irradiation and recrystallization.

light for 30 h. The absence of peaks for ethylenic protons and the presence of a multiplet peak for cyclobutane protons at δ 5.04 ppm in ^1H NMR spectrum confirm the formation of HT-dimer in quantitative yield (see ESI †). On the other hand, the anhydrous salt obtained by reacting with HPVBA and HCl in methanol was found to be photostable.

Photoreactivity of salts of HPVBA with diamines

The utilisation of $-\text{CO}_2\text{H}$ groups in various photoreactive olefins for making molecular salts and their photoreactivity is also reported in literature by us and others.^{4a-c,4g,4i,4k} Here, we attempted to exploit the carboxylic acid functionality of HPVBA by deprotonating the acidic proton by ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane. The flaky crystals obtained from these three diamines were studied for their photoreactivity and we found only the salt with 1,4-diaminobutane (**7**) underwent about 75% photodimerization in HT-fashion after UV irradiation for 40 h.

Ethylenediamine is known to template *trans*-cinnamic acid analogues that undergo photodimerization.^{4a} We also have shown that 1,3-diaminopropane can template H_2SDC for the same purpose but not ethylenediamine or 1,4-diaminobutane.^{4g,4i} Here, we observe that for HPVBA, 1,4-diaminobutane serves as a template but not the other two amines in the series. To our disappointment, all the crystals isolated were flaky and not suitable for intensity data collection to solve the structure by X-ray crystallography. However, these observations clearly indicate that there is definitely some correlation of crystal packing with the chain length of diamines and olefinic spacers. Any two hydrogen atoms in the $-\text{NH}_3^+$ groups can donate hydrogen bonding to two carboxylate groups, thereby clipping

two carboxylate-olefins into a parallel arrangement. However, we are unable to verify this experimentally.

A comparative discussion

Significant success has been achieved in the design of photoreactive co-crystals. However, there has been a little progress in understanding the nature of supramolecular interactions and solid state packing of the salts. Among the salts described above, the photoreactivity was observed randomly in an unpredictable manner in two ways. The first priority is to make the photoreactive salt and then the second concern is controlling the orientation *i.e.* whether in HH- or HT-fashion. In CF_3CO_2^- salt, two H_2PVBA^+ cations were clipped nicely, however the salt was photostable. On the other hand, ClO_4^- did not clip two H_2PVBA^+ cations, but the parallel arrangement was observed without any clipping and it was photoreactive in HT-fashion. The presence of methanol solvents in perchlorate salt has also been shown to have very crucial role for this salt to be photoreactive. It was reported earlier that the hydrochloride salts were photoreactive in HT-fashion for 4-PA and 4-styrylpyridine.^{4f,4j} However, this was not the case for HPVBA. The nitrate salt of 4-PA was photostable but the same salts of 4,4'-bpe^{4j,12} as well as HPVBA were found to be photoreactive. All these observations clearly indicate that it is quite a formidable task to predict the photoreactivity in the salts of pyridyl derivatives containing olefins with inorganic acids. Not only the pyridyl salts of inorganic acids but also the carboxylate salts of organic amines are difficult to be predicted or designed as we can see the results for ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane *etc.* It is also important to note that in many cases the salts are hydrated (or solvated) and the solvents have a crucial role in the photoreactivity. The reason behind this can

stem from the fact that the charge assisted hydrogen bonding in salts is less directional in nature compared to neutral hydrogen bonding in co-crystals. In addition to hydrogen bonding interactions, electrostatic interactions also influence solid state packing of salts. Therefore, the bonding interaction can form within a wide range of solid angles which causes them to be less predictable.¹³

One might argue that aligning two photoreactive C=C bonds in a parallel orientation in a salt is nothing but screening (trial and error) and may not be achieved by design. We expected HH-dimer from sulphate-bisulphate salt of HPVBA, however it surprisingly resulted in HT-dimer in this case; yet the HH-dimer was obtained serendipitously by incorporating excess H₂SO₄ during crystallization. Moreover, both the HH- and HT-dimers were obtained from the series of these salts by tuning the salt former and solvent of crystallization. Although, the predictability of solid state structure of salts is poor, salts have several advantages such as a) robust structure, b) higher thermal stability, c) better water solubility and d) ease of separation of the products after photodimerization just by simple acid-base work up. In addition, the pyridyl containing cyclobutane compounds undergo isomerization from *rectt*- to *rcct*- isomers in solution providing access to more cyclobutane compounds as ligands. Therefore, organic salts deserve more attention especially in the solid state photodimerization and isomerisation reactions in order to assess their usefulness in green synthesis.

Co-crystal of *rectt*-HT-4,4-BPCD with 4,4'-bpe

For crystallographic characterization, both these cyclobutane compounds *rectt*-HH-4,4-BPCCB and HT-4,4-BPCCB were

employed to make co-crystals with dipyrindyl spacer compounds, however we were only successful in obtaining the single crystals of (HT-4,4-BPCCB)(4,4'-bpe) from the evaporation of an equimolar solution of 4,4'-bpe and HT-4,4-BPCCB in 1 : 4 DMF and methanol mixture. Single crystal X-ray diffraction analysis revealed that HT-4,4-BPCCB adopted *rectt*-conformation in the co-crystal (HT-4,4-BPCCB)(4,4'-bpe)(MeOH)_{0.75}(H₂O)₂ (**8**). From the observed values of C=O distances for two carboxylic acid groups [C=O distances are 1.23(5) and 1.21(5) Å, respectively, and both the corresponding C–OH distances are 1.32(5) Å], it can certainly be called a co-crystal and not a salt. The two carboxylic acid groups donate H-bonding to two pyridyl groups in R₂²(7) and C(2) fashion as shown in Fig. 6. The keto oxygen of the carboxylic acid group interacts with methanol molecules with O...O distance of 2.946 Å but with O–H...O angle of 115.6°, this may not be significant for H-bonding. But, one pyridyl group accepts H-bonding from a methanol molecule with N...O distance of 2.77 Å and N...H–O angle of 137.2°. Meanwhile the other pyridyl group has interaction with water molecule maintaining N...O distance of 2.86 Å, but these interactions may not be significant as the N...H–O angles are 87.7° and 75.9°. Similarly, the distance between two water molecules (O...O distance of 2.88 Å) suggest bonding interaction, but the positions of H atoms do not. Among two water molecules present, the hydrogen atoms of one could not be located. As the growth of H-bonded network is interrupted by the solvent molecule, the overall structure of this co-crystal was determined to be one dimensional.

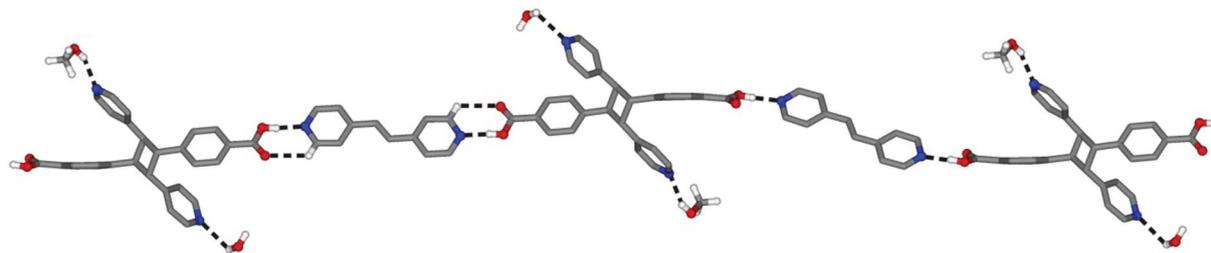
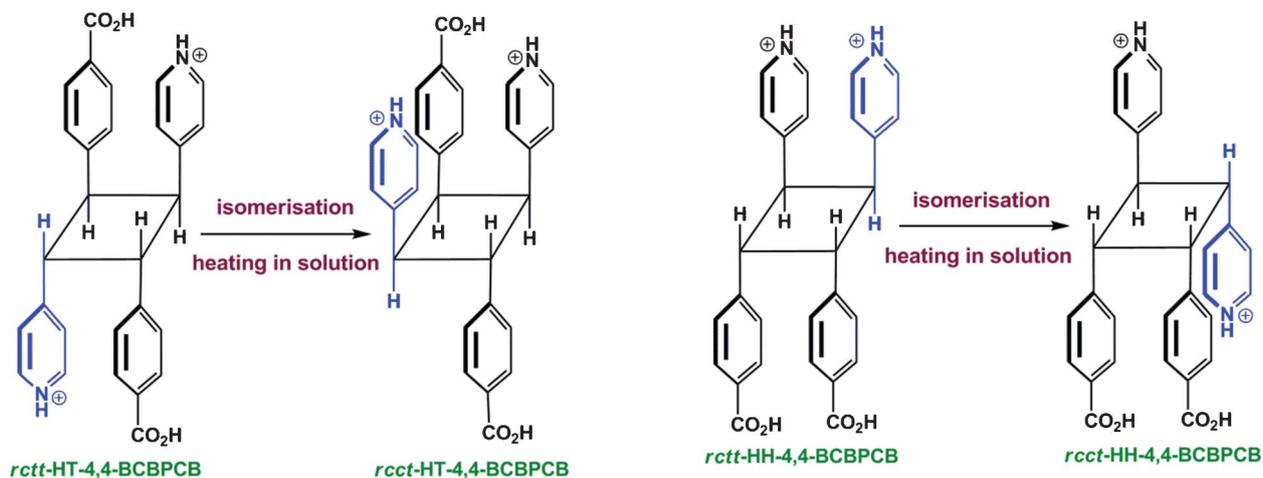


Fig. 6 One dimensional hydrogen bonded chain of **8**. The C–H hydrogen atoms are omitted.



Scheme 1 The structures of the *rectt*- and *rcct*-isomers of HT and HH-4,4-BCBPCB.

Isomerisation of HH-BCBPCB and HT-BCBPCB

The acid catalysed isomerisation of *rcct*-4,4-tpcb to *rtct*-tpcb and the isomerisation of *rcct*-HH-4,4-BPCD and *rcct*-HT-4,4-BPCD to their corresponding *rcct*-isomers have been reported from our laboratory^{Aj,7b,14} and by Briceño.^{5e,15} The above two cyclobutane compounds were also observed to undergo similar isomerisation from *rcct*- to *rcct*- isomers under acidic pH, which was observed to be faster upon heating. The ¹H NMR spectrum confirming the isomerisation for HH-dimer is shown in ESI† and the structures of the corresponding *rcct*-isomers are shown in Scheme 1. Two doublet peaks for cyclobutane protons for *rcct*-HH-4,4-BCBPCB converts to four triplet peaks upon heating, which indicate that the degeneracy of the cyclobutane protons is lifted due to isomerisation to *rcct*-isomer (symmetry reduced). We also observed that the isomerisation is not quantitative because the product *rcct*-isomer is less stable than *rcct*-isomers as there are three substituents on the same side of the cyclobutane ring resulting in steric hindrance. The *rcct*-HT-4,4-BCBPCB also undergoes similar isomerisation under similar conditions as was observed in ¹H NMR spectroscopy (see ESI†).

Conclusion

We have discussed several salts of HPVBA obtained by reacting with inorganic acids and organic diamines, and they were investigated for their photoreactivity. Both the HH- and HT-dimers of this unsymmetric olefin were obtained stereoselectively. It has been shown that the solvents present in the salts play a crucial role in their photoreactivity. More interestingly, both the HT- and HH-dimers could be obtained from same salt former, H₂SO₄, just by changing its concentration during crystallization. Such flipping of orientation from HT- to HH-arrangement by single salt former was not known before. Although the predictability of solid state structure of salts is poor, it is shown that the strategy of salt formation works well in organic synthesis and it warrants much more attention to understand how two ionic counterparts combine and construct the solid state packing in salts to gain credibility in crystal engineering.

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