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PAPER

Solid state double [2 + 2] photochemical reactions in the co-crystal forms of 1,5-bis(4-pyridyl)-1,4-pentadiene-3-one: establishing mechanism using single crystal X-ray, UV and ^{1}H NMR†

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Double [2 + 2] photochemical reaction of 1,5-bis(4-pyridyl)-1,4-pentadiene-3-one (**1P**) was observed with 100% yield in four co-crystal forms of **1P** with the hydrogen bonding template molecule phloroglucinol (PG) or 5-methoxy resorcinol (MR). The crystal structure of compound **1P** does not have the required geometry to produce the double [2 + 2] reaction product, but it gives a single [2 + 2] reaction product with 15% yield upon time restricted irradiation. All the reactions in co-crystals of **1P** resulted in the stereospecific *exo–exo* tetrapyridyl tricyclo[6.2.0.0^{3,6}]-decane. ^{1}H NMR and the UV-vis spectroscopic studies clearly established a stepwise mechanism for this reaction through the formation of monocyclobutane intermediate. One co-crystal form of **1P** with PG and another co-crystal form of **1P** with resorcinol were found to be unreactive due to different reasons. Furthermore the mechanochemical grinding products of **1P** with RN or MR have exhibited similar structural and reactivity correlations with those crystallized from solution.

Introduction

The chemical reactions in the solid state offer stereo- and regiochemical control as the environment around the reactive functional groups is well defined due to the restricted molecular movements.[1,2] Various photochemical reactions such as [2 + 2] dimerization or polymerization, Norish/Yang-type I or II[3] and di-π-methane rearrangements[4] are some of the popular reactions in solid state chemistry.[5] Among these, [2 + 2] reactions are well studied by Schmidt and he postulated a set of rules by systematically exploring several substituted olefins.[1] However, many examples of olefins have been reported which violate Schmidt's topochemical principles of [2 + 2] reactions.[6] More often such violations were attributed to the varied degree of molecular motions within the crystal lattice. The newly gained knowledge on various intermolecular interactions and the identification of a variety of supramolecular synthons[7] had given an impetus to re-examine the photochemical reactions of olefins which have unreactive geometries.[8] Therefore, the syntheses of co-crystals or metal complexes of olefins were seen as a means for re-orienting the double bonds to reactive geometries. Some of the interactions which are in use for this purpose are strong hydrogen bonds,[9] coordination bonds,[10] halogen bonds[11] and metal···metal interactions.[12] In particular the approach of MacGillivray *et al.* for bringing two bis-pyridyl ethylene molecules within the reactive distance by clipping them with various resorcinol derivatives *via* O–H···N hydrogen bonds has gained a special attention.[9] Also the resultant tetra-pyridyl products from such reactions are of importance for constructing various functional MOFs.[13] Therefore [2 + 2] reactions with the simplest bis-pyridyl olefin, *i.e.* 1,2-bis(4-pyridyl)ethylene, have been reported by several groups using different crystal engineering strategies.

Various substituted dienes are also of importance for [2 + 2] reactions due to the possibility of formation of tricyclic derivatives in stereo-selective manner which are otherwise difficult to synthesize. Symmetrically substituted pentadiene-3-one is one such example which contains two olefins separated by a carbonyl group. In this paper we aim to study the photochemical [2 + 2] reactions of **1** with R = 4-pyridyl (**1P**). Molecule **1** can exhibit three stable conformations (Scheme 1), therefore in principle it is possible to obtain different stereo- and regio-selective dimeric products by arresting various conformations in the co-crystals of **1P** with di-hydroxy and tri-hydroxy benzenes. We note here that previously the photochemical reactions of 1,4-pentadiene-3-one moiety with R = –COOH, 3,4-dichlorophenyl or –COOMe have been studied and found to produce the *exo–exo* tricyclo[6.2.0.0^{3,6}]-decane (*exo–exo* TCD) ring system upon photochemical irradiation, while **1** with R = phenyl, that is dibenzylidene acetone, was shown to be photochemically

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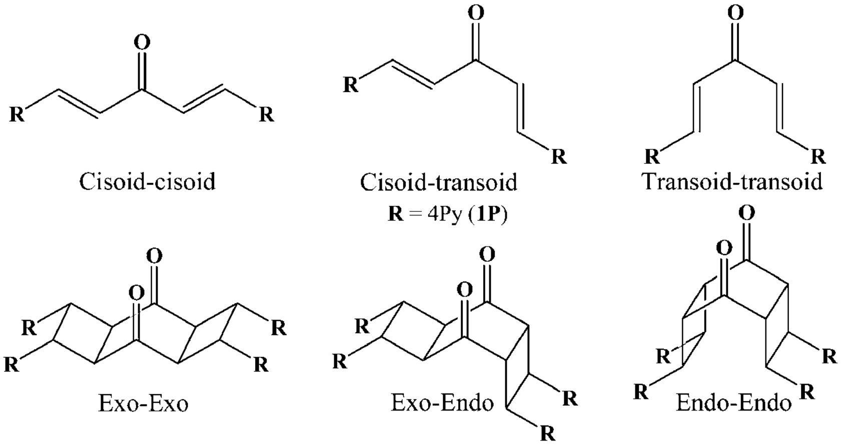
† Electronic supplementary information (ESI) available: Other geometrical parameters for all the reactive double bonds in the co-crystals, IR spectra, ^{1}H NMR spectra, ^{13}C NMR spectra, XRPD patterns, and crystallographic data for compounds **4–8** in CIF. CCDC reference numbers 688735 and 793077–793080. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00612b



Scheme 1 Three possible conformations of **1** and respective (TCD) products upon double [2 + 2] photochemical reaction.

unreactive.[14] Further while studying the photochemical reaction of **1** with R = 3,4-dichlorophenyl, Green and Schmidt have proposed two possible pathways for this reaction and tried to establish the mechanism by irradiating the compound at different wavelengths (Scheme 2). Their efforts to isolate or to identify the formation of single photochemical reaction product (monocyclobutane, MCB) were unsuccessful; therefore they have concluded that the reaction may be proceeding through the other root in which both the double bonds react simultaneously.

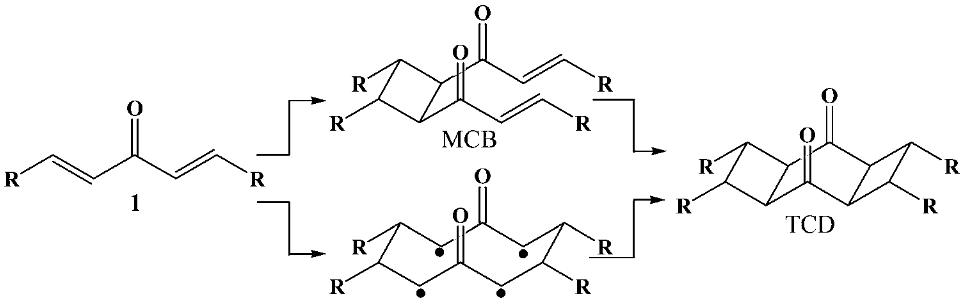
In contrast to the above observations, our study on the photochemical reactivity of **1P** in the co-crystal of **1P** with phloroglucinol indicates that the reaction proceeds through stepwise mechanism.[15] This aspect was proven by us using single crystal X-ray diffraction and ^{1}H NMR spectra. In this manuscript we aim to see the generality of such step-wise mechanism in the various related co-crystals of **1P** and also aim to explore the possibility of obtaining different stereo- and regio-isomeric dimers. Accordingly, we describe here our studies on topochemical reactions in four more co-crystals of **1P**. Further the double [2 + 2] reactions in all these co-crystals have been monitored by ^{1}H NMR and UV-vis spectroscopy to establish the mechanism. The possibility to synthesize these co-crystals of **1P** *via* mechanochemical grinding and thereby the photochemical reactivity of such co-grounded solids will also be addressed in this article.

Results and discussion

Compound **1P** was synthesized from acetone-1,3-dicarboxylic acid and 4-pyridinecarboxaldehyde following the literature procedure.[16] The crystals of **1P** were obtained from toluene and found that the double bonds are not aligned in the required fashion for double [2 + 2] photochemical reaction.[15] Therefore the compound **1P** has been co-crystallized with resorcinol (RN), phloroglucinol (PG) and 5-methoxy resorcinol (MR) from various solvents and mixtures of solvents. Only one crystalline form (**1P**·RN, **2**) was obtained for the co-crystals of **1P** with resorcinol in spite of several crystallization trials from different solvents. In contrast, various crystallization reactions with PG and **1P** resulted in a total of four crystalline forms: [**1P**·PG·CH_3CN], **3**; [4(**1P**)·3PG·4H_2O], **4**; [2(**1P**)·PG·4H_2O], **5** and [**1P**·PG], **6**. Similar to RN, MR also forms only one crystalline form [2(**1P**)·2MR·H_2O], **7**. The crystal structures of **1P** and co-crystals **2–7** were determined and analyzed in terms of their double bond geometries, hydrogen bonding interactions and photochemical reactivity. Pertinent crystallographic details, hydrogen bonding interactions, and geometrical parameters for the alignment of double bonds with the photochemical reaction details are given in Tables 1–3 respectively.

Topochemical reactivity of 1P

Among the three possible isomers of **1P**, the transoid–transoid isomer deviates from linearity and also it is least stable due to steric interactions between the β-hydrogens. The CSD search on the aromatic substituted compounds with the 1,4-pentadienone moiety shows that ten out of fourteen structures exhibit cisoid–cisoid conformation, three exhibit cisoid–transoid and only one exhibits transoid–transoid conformation. These statistics



Scheme 2 Schematic representation for the possible intermediates of double [2 + 2] reaction of **1**.

Table 1 Crystallographic parameters for the crystal structures of **4–8**[a]

Compound	**4**	**5**	**6**	**7**	**8**
Formula	$C_{78}H_{74}N_8O_{17}$	$C_{36}H_{38}N_4O_9$	$C_{21}H_{18}N_2O_4$	$C_{22}H_{21}N_2O_{4.25}$	$C_{30}H_{24}N_4O_2$
MW	1395.45	670.70	362.37	381.41	472.53
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	$P\bar{1}$	*C*2/*c*	*P*2(1)/*n*
a/Å	19.3013(16)	12.873(2)	8.6268(9)	12.091(2)	15.178(5)
b/Å	15.3054(13)	15.947(3)	9.6019(10)	14.993(3)	6.090(2)
c/Å	23.9379(19)	16.881(3)	12.1252(13)	22.115(4)	26.470(8)
α/°	90.00	90.00	76.149(3)	90.00	90.00)
β/°	122.935(4)	90.206(5)	88.030(3)	97.250(5)	102.280(10)
γ/°	90.00	90.00	67.701(3)	90.00	90.00
Vol./Å^3	6971.4(10)	3465.4(10)	900.46(16)	3977.2(11)	2390.9(13)
Z	4	4	2	8	4
D_{calc}/Mg m^{-3}	1.330	1.286	1.337	1.287	1.313
R_1 ($I > 2\sigma(I)$)	0.0592	0.0637	0.0408	0.0808	0.0761
wR_2 (on F^2, all data)	0.1901	0.1919	0.1416	0.2245	0.2028

[a] Crystallographic parameters for crystal structures of **1P**, **2**, **3** and **9–11** are published in our previous communication.

indicate that even in the crystal structures the probability of exhibiting least stable isomer is very less while the probability for the most stable isomer is significantly high.

Notably none of these compounds were reported to exhibit conformational polymorphs. Recently a somewhat structurally related diene molecule, 1,3-bisstyrylbenzene dicarboxylic acid,

Table 2 Some significant hydrogen bond interactions in the structures of **1P** and **2–11**[a]

Comp.	Interaction	H···A/Å	D···A/Å	D–H···A/°
1P	C(12)–H(12)···O(32)[a]	2.50	3.2405(17)	137
	C(26)–H(26)···N(21)[b]	2.61	3.4703(17)	154
2	O(2A)–H(2A)O···N(11)[c]	1.829(19)	2.753(2)	174.4(17)
	O(1A)–H(1A)O···N(21)	1.87(3)	2.759(2)	161(3)
3	O(1)–H(1)O···N(21)[d]	1.86(4)	2.761(3)	177(3)
	O(3)–H(3)O···N(31)[e]	1.94(3)	2.803(3)	171(3)
	O(5)–H(5)O···N(100)	2.03(3)	2.828(3)	162(3)
4	O(1E)–H(1)···N(11B)[f]	1.68	2.648(3)	154
	O(3E)–H(2)···N(11A)[g]	1.62	2.672(3)	177
	O(5E)–H(3)···N(21D)[g]	1.57	2.631(3)	179
	O(1F)–H(4)···N(11C)[h]	1.82	2.715(3)	178
	O(3F)–H(5)···O(3)W	1.71	2.641(3)	175
	O(5F)–H(6)···N(21B)[h]	1.87	2.735(3)	174
	O(1G)–H(7)···N(21A)[i]	1.77	2.816(3)	172
	O(3G)–H(8)···O(1)W	1.61	2.680(3)	175
	O(5G)–H(9)···N(11D)[i]	1.88	2.751(3)	178
5	O(1)–H(1)O···O(1)W	1.94	2.800(3)	170
	O(2)–H(2)O···N(31A)[j]	2.02	2.833(3)	176
	O(3)–H(3)O···N(21B)[k]	1.85	2.705(3)	175
6	O(1)–H(1)O···O(10)	2.04	2.888(10)	160
	O(1)–H(1)O···O(10A)	1.81	2.684(11)	166
	O(2)–H(2)O···N(11)[l]	1.76	2.7186(19)	170
	O(3)–H(3)O···N(21)[m]	1.86	2.7729(19)	175
7	O(31)–H(31)O···N(11)[n]	1.94	2.815(4)	170
	O(33)–H(33)O···N(21)[o]	2.03	2.735(4)	170
8	C(12B)–H(12B)···O(1B)[p]	2.37	3.248(5)	157
	C(14A)–H(14A)···O(1A)[q]	2.47	3.354(5)	158
	C(25A)–H(25A)···N(11B)[r]	2.58	3.455(6)	156
9	O(1A)–H(1A)O···N(21)	1.80(4)	2.755(4)	170(3)
	O(3A)–H(3A)O···N(11)[s]	1.76(4)	2.765(4)	176(3)
	O(2A)–H(2A)O···N(100)	1.94(5)	2.810(5)	164(4)
10	O(1A)–H(1A)O···N(100)[t]	1.92(6)	2.811(7)	153(4)
	O(3A)–H(3A)O···N(11)[u]	1.76(6)	2.747(6)	172(5)
	O(2A)–H(2A)O···N(21)[v]	1.74(8)	2.772(6)	168(7)
11	C(13B)–H(13B)···N(21A)[w]	2.44	3.272(4)	142
	C(22B)–H(22B)···O(100)[x]	2.54	3.384(6)	152

[a] Symmetry code: [a]–1/2 + x, 1/2 – y, –1/2 + z; [b]–1/2 + x, –1/2 – y, –1/2 + z; [c]2 + x, 1/2 – y, –1/2 + z; [d]–x, 1 – y, –z; [e]–1 + x, 1 – y, –1/2 + z; [f]–1 + x, 1/2 – y, –1/2 + z; [g]1 – x, –1/2 + y, 1/2 – z; [h]-x, 1 – y, –z; [i]1 + x, 1/2 – y, 1/2 + z; [j]1 + x, 1/2 – y, 1/2 + z; [k]x, 1/2 – y, 1/2 + z; [l]–x, 1 – y, –z; [m]2 – x, –y, 1 – z; [n]–1/2 – x, 1/2 – y, –z; [o]–1/2 + x, 1/2 – y, –1/2 + z; [p]x, –1 + y, z; [q]x, 1 + y, z; [r]3/2 – x, –1/2 + y, 1/2 – z; [s]2 – x, y, 3/2 – z; [t]1 – x, –y, 1 – z; [u]x, 1 – y, –1/2 + z; [v]x, 1 – y, –1/2 + z; [w]–1/2 – x, –1/2 + y, 3/2 – z; [x]–1/2 + x, –1/2 – y, 1/2 + z.

was shown to exhibit such conformation related polymorphic forms and thereby results in various isomeric dimers or polymers upon irradiation.[17]

Compound **1P** has been crystallized from a variety of solvents and solvent mixtures in anticipation of polymorphs or various solvates. However, it always resulted in a unique crystalline form in which the molecule **1P** exhibits cisoid–transoid conformation (Fig. 1). The pentadienone moiety exhibits near planarity while the pyridyl rings make angles of 21.51° and 11.34° with the plane of double bonds. In the lattice the molecules join *via* C–H···N and C–H···O hydrogen bonds to form a two-dimensional layer. The molecules stack on each other such that each one of the molecule has two types of interactions: one side of the molecule has offset arrangement in which cisoid double bonds are parallel and satisfy Schmidt's criteria for [2 + 2] topochemical reaction (Table 3) while the other side of the molecule interacts with inversion related molecule such that the double bonds have crisscross alignments with the centroid-to-centroid distance of 3.84 Å (Fig. 1b–d).

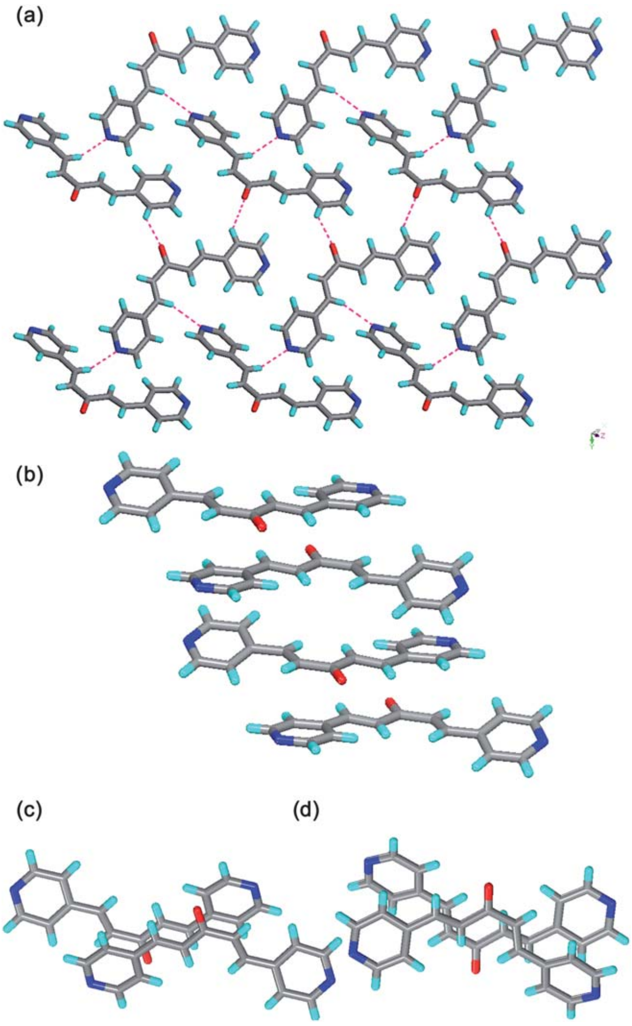


Fig. 1 Illustrations for the crystal structure of **1P**: (a) 2D layer through weak C–H···O and C–H···N hydrogen bonds; (b) two types of π-stacks of **1P**; (c) offset and (d) crisscross arrangement (top view).

The grinded crystalline material of **1P** was irradiated in sunlight by placing the material between two thin glass plates. The ^{1}H NMR spectra after one day of irradiation in the sunlight show peaks corresponding to cyclobutane derivative **8** along with several other uncharacterized peaks that are presumably corresponding to oligomers or polymers. Further irradiation of this mixture resulted in only oligomers and polymers but not dimeric compound **8**. Therefore, after irradiation of **1P** for a day, the compound **8** was separated in 15% yield as a white solid by crystallizing the reaction mixture from acetone–methanol. Suitable single crystals of **8** for X-ray diffraction were grown from methanol. Crystal structure analysis shows that **8** contains a dimer with the stereochemistry expected from offset arrangement (Fig. 2). In the crystal structure of **8**, the molecules form a 1D chain through a bifurcated C–H···O hydrogen bonds of the cyclobutane C–H and β-H of pyridine with the carbonyl oxygen. These chains interact with each other *via* weak C–H···N interactions to yield a three-dimensional packing.

Unreactive co-crystals

The co-crystals **2** and **6** were found to be unreactive for different reasons. In the co-crystal **2** the RN moieties do not act as a clip to bring the two units of **1P** within the photochemical reactive distance. The RN exhibits divergent geometry with two –OH groups pointing away from each other.

As a result it forms 1D-chains *via* O–H···N hydrogen bonds (Fig. 3). These chains pack through weak interactions such that the double bonds do not contain reactive alignments.

The co-crystal **6** (**1P**·PG) is one of the four co-crystals of PG with a unique quality of not having any solvent in the crystal lattice. The crystal structure analysis of **6** reveals that PG exhibits the required conformation to act as a template but it

Table 3 Geometrical parameters for the alignment of double bonds and photochemical reaction details for compound **1P** and **3–7**

Comp.	distances	C=C···C=C torsion	Irradiation time in sunlight	Max. yield of product
1P	3.88 Å, 3.84 Å, 4.00 Å	~0°, ~61.5°	1 day	~15% of **8**
3	3.60 Å, 3.85 Å	~3.65°	3–4 h	~100% TCD
4	3.62 Å, 3.71 Å, 3.63 Å, 3.72 Å, 3.63 Å, 3.66 Å, 3.52 Å, 3.73 Å	~3.63°, ~3.97°, ~5.42°, ~2.52°	2 days	~100% TCD
5	3.63 Å, 3.74 Å, 3.64 Å, 3.76 Å	~0.66°, ~3.16°	1 day	~100% TCD
6	3.61 Å	~0°	3 days	No reaction
7	3.69 Å	~15.36°	5–6 h	~100% TCD

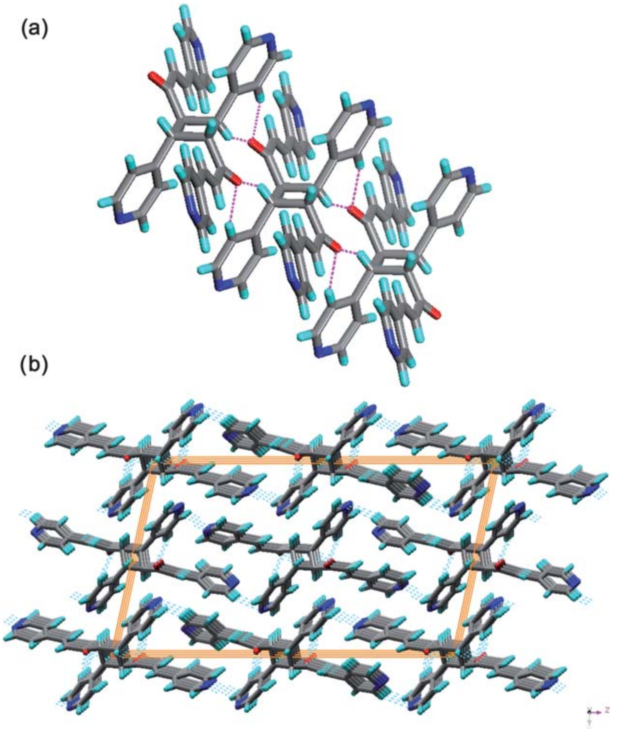


Fig. 2 Illustrations for the crystal structure of **8**: (a) 1D chain through bifurcated C–H···O hydrogen bonds; (b) packing of molecules.

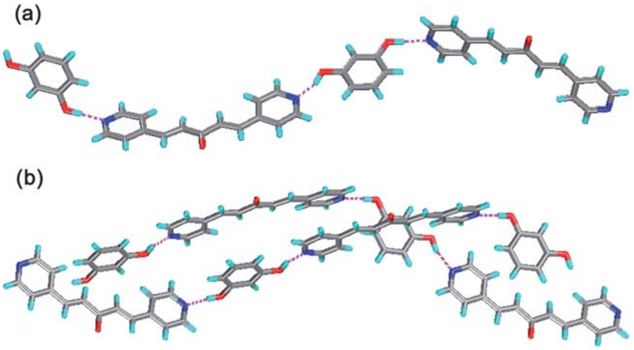


Fig. 3 Illustrations for the crystal structure of **2**: (a) 1D chain through O–H···N hydrogen bonds; (b) packing of two such 1D chains showing no alignments of double bonds.

does not clip the molecule **1P** in a required fashion to give the double [2 + 2] reaction (Fig. 4). The molecule **1P** exhibits cisoid–transoid and cisoid–cisoid geometry with 50% of occupancy each. In the crystal structure, two O–H···N hydrogen bonds and one O–H···O=C hydrogen bond between **1P** and PG lead to the formation of a double chain in which the cisoid (non-disordered) double bonds satisfy the Schmidt's criteria to yield the photodimer **8**. However, it was found that the co-crystal **6** is photostable and no reaction occurs even after irradiation for many days. Although double bonds satisfy the required geometrical criteria (Table 3) the lack of required molecular motions and disorder within the crystal lattice could be a possible reason for the observed unreactivity.

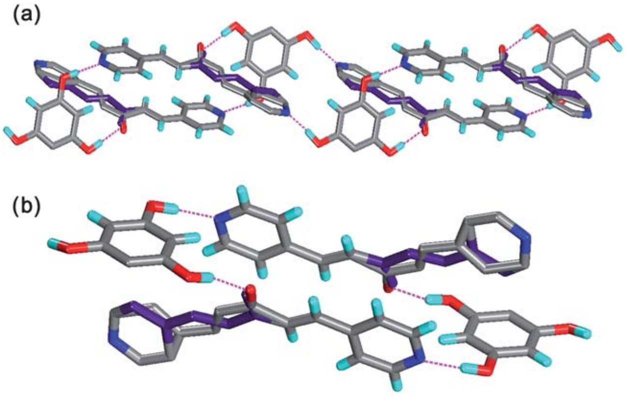


Fig. 4 Illustrations for the crystal structure of **6**: (a) 1D chain through O–H···N and O–H···O (O=C) hydrogen bonds; (b) alignment of cisoid double bonds of **1P** in such 1D chain.

Double [2 + 2] reaction in co-crystals of 1P with phloroglucinol

The contents of asymmetric units in the co-crystals of **3–5** are as follows: **3** contains one each of acetonitrile, PG, and **1P**; **4** contains four molecules of **1P**, three molecules of PG and four molecules of water; **5** contains two molecules of **1P**, one molecule of PG and four molecules of water. The molecule **1P** exhibits cisoid–cisoid conformation in the co-crystals of **3** and **4**, while it exhibits cisoid–transoid conformation in the co-crystals of **5** (Fig. 5). In **3**, two –OH groups of PG clip two molecules of **1P** *via* O–H···N hydrogen bonds as anticipated and the third –OH group of PG interacts with CH_3CN *via* O–H···N hydrogen bonds. While in **4**, two types of clipping were found: the first type is identical to the one observed in **3** and in the second type of clipping one side of the two π-stacked moieties of **1P** is clipped by PG whereas the second side is clipped by PG and two water molecules. In **5**, the two π-stacked units of **1P** are clipped in required fashion but one side (cisoid side) by the PG and the other side (transoid side) by the three water molecules. In all three co-crystals the double bonds satisfy the required topochemical criteria for [2 + 2] photochemical reaction (Table 3). From the geometries of the supramolecular π-stacks of **1P** in the co-crystals, it was anticipated that **3** and **4** should yield *exo–exo* TCD and **5** should yield *exo–endo* TCD. In contrast the photochemical irradiation of all three co-crystals yielded *exo–exo* TCD. Also, the reactivity of these compounds was found to differ significantly. The compounds **3** and **5** react even in room light while the compound **4** reacts only either under sunlight or UV light. Further, the crystals of **3** were found to be intact during the entire process of the reaction. In contrast the crystals of **4** and **5** loose the crystalline nature during the irradiation, may be due to the loss of lattice water. The loss of water in **5** may also explain the non-correlation of reactant geometry with the product geometry. As mentioned before one end (transoid) of the π-stacked dimers of **1P** was tied by the H_2O molecules. The loss of these H_2O molecules triggers the rearrangement of double bond to cisoid conformation, which can be termed as a pedal motion, resulting in *exo–exo* TCD. Generally, pedal motion causes orientation of crisscrossed double bonds into the parallel alignments or an isomerization of double bonds. In the co-crystal **5**, the driving force for such pedal motion might be the conversion of unstable conformer into the stable conformer of **1P**.

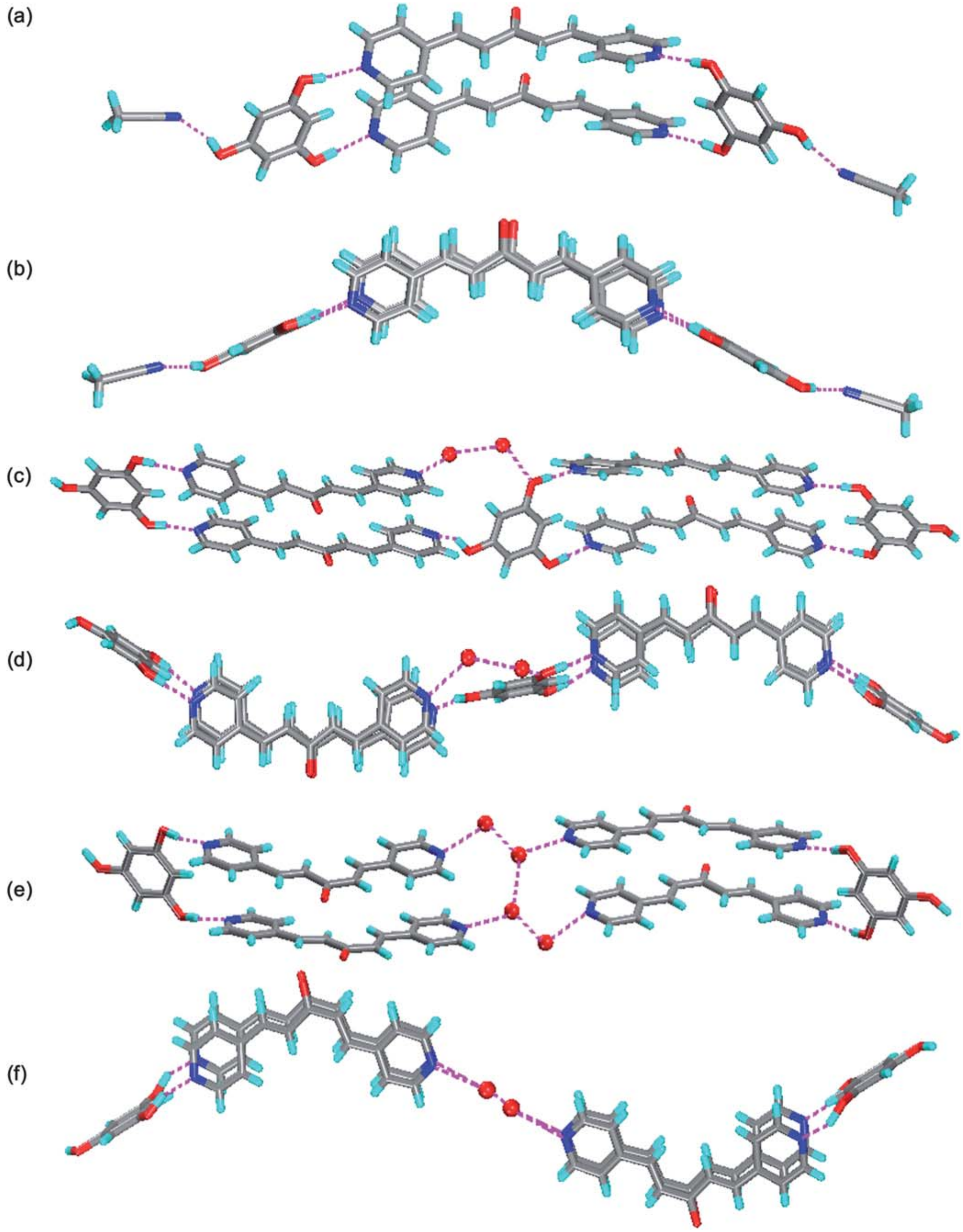


Fig. 5 Illustrations for the crystal structures of **3**, **4**, and **5**: (a) supramolecular templated unit in **3** through O–H···N hydrogen bond; CH_3CN forms O–H···N hydrogen bond with the third –OH group of PG and (b) side view; (c) supramolecular unit showing the dimeric stacking of **1P** in **4** and (d) side view; (e) supramolecular dimeric stacking of **1P** in **5** through the H-bonding by PG and water molecules and (f) side view; notice the difference in geometry of **1P**.

Double [2 + 2] reaction in the co-crystal of 1P with methoxy resorcinol

The failed clipping of **1P** units by resorcinol in **2** and the unreactivity of the co-crystal **6** prompted us to investigate the reaction of **1P** in another system by considering 5-methoxy resorcinol. It is important to note here that MacGillivray *et al.* have demonstrated that the substitution at C-5 position of resorcinol increases the probability of resorcinol to exhibit ideal clipping geometry. Therefore we have considered 5-methoxy resorcinol (MR) to complex with **1P**. Our results suggest that this complexation reaction unlike PG results in only one crystalline form [2(**1P**)·2MR·H_2O], **7**. The asymmetric unit of **7** contains one each of **1P** and MR and half unit of water. The molecule MR exhibits the required clipping geometry and clips two units of **1P** *via* O–H···N hydrogen bonds (Fig. 6). The alignments of double bonds satisfy the required geometrical criteria for topochemical reactivity (Table 3). The irradiation of the material resulted in the 100% conversion of **1P** into TCD as suggested by ^{1}H NMR.

Single crystal-to-single crystal transformations

The co-crystals of **3** and **7** were found to undergo [2 + 2] reactions retaining the crystalline nature.[18] However, among these only the

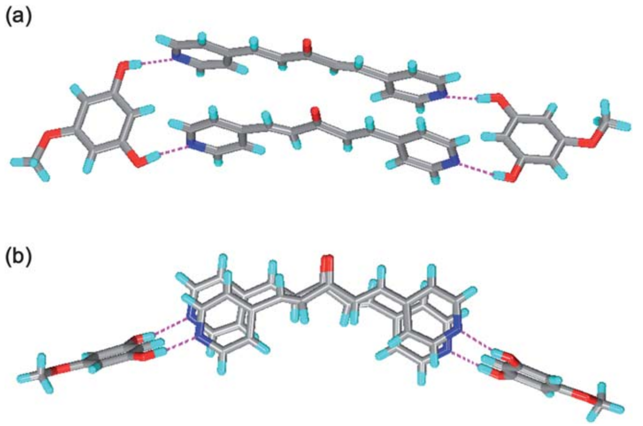


Fig. 6 Illustrations for the crystal structure of **7**: (a) supramolecular templated unit of **1P** by MR through O–H···N hydrogen bonds and (b) side view.

co-crystals of **3** were found to be intact as a single crystal without breaking into small pieces during the entire process. The single crystal X-ray analyses of the irradiated crystals of **3** were performed after partial irradiation (**9**) and also after complete irradiation (**10**). The yellow crystals of **3** turn to colorless crystals (**10**) after the complete conversion to TCD. The cell parameters of **9** and **10** are almost similar to those of **3** with some minor differences.[15] The crystal structure of **9** reveals that 60% of the double bonds are reacted and 40% of the double bonds are unreacted (Fig. 7). Therefore **9** exhibits a disorder in the form of two sets of coordinates: one set corresponds to an unreacted double bond with 40% occupancy while the other set corresponds to cyclobutane with 60% occupancy. The pyridyl groups exhibit only single orientation representing those of the product and the un-reacted component. As a consequence of the single orientation of the pyridyl groups, some distortion occurred in the C(Py)–C(Py)–olefinic or cyclobutane angles. However from this structure, it is difficult to conclude whether the observed disorder is due to the presence of the products of single [2 + 2] and/or double [2 + 2] and/or unreacted components.

The crystal structure analysis of fully reacted crystals (**10**) reveals that the crystal packing mostly remains intact. However, huge geometrical differences were observed between the supramolecular dimer observed in **3** and covalent dimer (TCD) of **1P** (Fig. 7c) observed in **10**. The newly formed C–C bonds in TCD have the bond lengths of 1.619(7) and 1.607(7) Å. The C-atoms of carbonyl carbons are much closer (2.663 Å) in TCD than in the supramolecular dimer (3.631 Å). The distance between the N-atoms of the pyridine rings which are hydrogen bonded to same PG molecule slightly increases in **10** compared to that in **3** (4.504 *vs.* 4.128 Å). Further the interplanar angles between these pyridyl rings also differ significantly, they are more parallel in TCD (7.87°) than those in supramolecular dimer (33.7°). These parameters indicate that the significant changes occurred in the crystal lattice during the transformation. Despite such huge differences between supramolecular dimer and TCD, the hydrogen bonds remain same in both the structures. More interestingly, solvated CH_3CN remains in the crystal lattice during the entire reaction process.

Stepwise dimerization, evidenced by monitoring through ^{1}H NMR

Our preliminary investigation on the photochemical reaction of **3** by ^{1}H NMR at various stages of reaction clearly indicated that

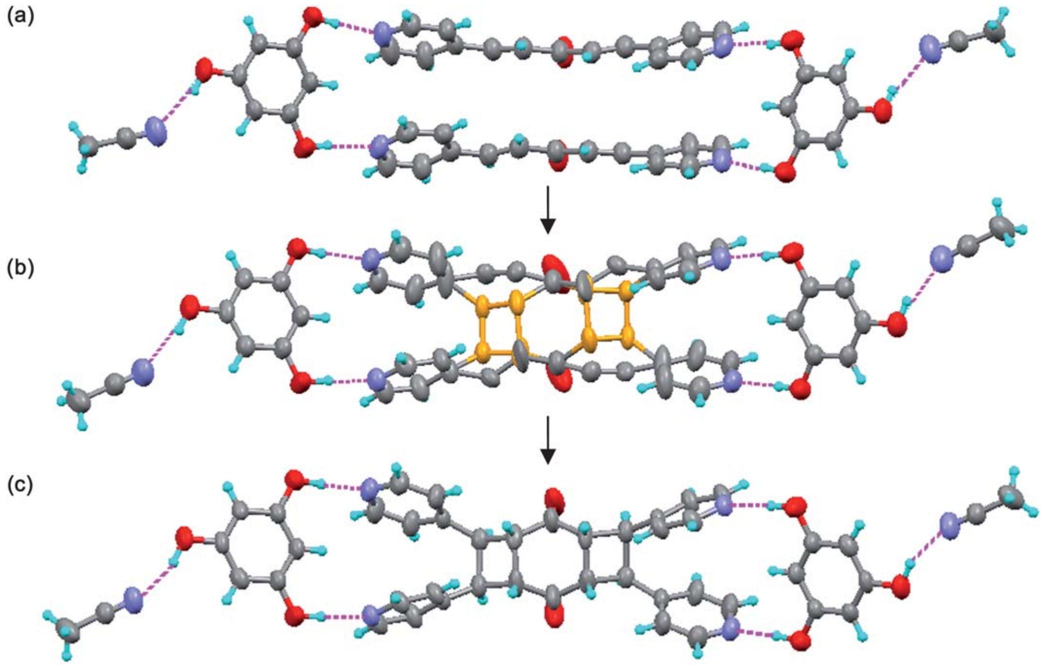


Fig. 7 Illustrations for the crystal-to-crystal conversion of **1P** to TCD: (a) supramolecular dimer of six components in **3** (b) after partial reaction, two sets of atom positions are identified for both olefin (gray) and cyclobutane (yellow) in **9**; (c) after complete conversion, TCD molecule retains the hydrogen bonding with PG (**10**) in spite of significant structural changes.

the reaction is indeed stepwise.[15] Similarly, here we have monitored photochemical irradiation of co-crystals **4**, **5**, and **7** by ^{1}H NMR spectroscopy in anticipation of identifying the intermediate MCB. The ^{1}H NMR spectra after partial irradiation of these co-crystals showed two new doublets (δ 4.295 and 4.784) in the cyclobutane proton region in addition with the anticipated doublets for cyclobutane ring corresponding to TCD (δ 4.429 and 4.642). These two new peaks were attributed to the cyclobutane protons of MCB. Further, two new doublets (δ 7.554 and 7.121) were observed in the upfield region (δ 7.778 and 7.559 for **1P**) corresponding to the double bonds of the intermediate MCB. The peaks corresponding to pyridine -αH and -βH were observed as four different doublets in new positions when compared to two doublets for pyridyl proton of **1P** and TCD. The splitting patterns and coupling constants of these new peaks clearly demonstrate the stepwise mechanism of the reaction with formation of intermediate MCB, and also excludes the formation of other radical intermediate. However, when the irradiation was carried out in the sunlight the major constituents at the various stages of the reaction are **1P** and/or TCD. Therefore at all stages the intermediate MCB were found to be present as a very minor component. This observation suggests that the formation of TCD from MCB is faster (sunlight) than the formation of MCB from **1P**. Therefore we have monitored the reaction by keeping in the room light. The exposure of the crystals of **3** on watch glass in the room light leads to the initial formation of small amount of single dimer (MCB), 47% was converted into MCB after first two days of exposure which was observed to increase further to 62% after two more days. In these four days, no trace of a double dimer was found, but after two more days of exposure a trace of double dimer appears. After a total of 15 days, the reaction mixture accounts for 81% of the intermediate MCB and 19% of the product TCD of double [2 + 2] reaction. With regard to the other co-crystals, crystals of **7** were found to be reactive in room light but relatively slower than those of **3**. The co-crystals of **5** were found to react even more slowly while those of **4** are almost unreactive. Therefore we have monitored the reactions of co-crystals **5** and **7** in the room light by recording ^{1}H NMR spectra at various stages of irradiation (Fig. 8 and 9). In both cases, initially the intermediate MCB was found to be a major product which gradually converts into TCD as reaction progresses. However in the case of **5**, the concentration of MCB was found to be less compared to those of **3** and **7**. The maximum concentration of MCB was observed up to 81%, 34% and 57% for **3**, **5** and **7** respectively.

Stepwise dimerization, evidenced by monitoring through UV

The reactions of **3**, **5** and **7** by exposing to the room light were also monitored using the UV-vis spectroscopy. The conjugation of double bond with the pyridyl group decreases from monomer **1P** to intermediate MCB to the final product TCD, therefore a gradual blue shift in their absorption maxima (λ_{max}) values is expected as the reaction progresses. The absorption spectra were recorded by dissolving 0.0403 mg, 0.0311 mg and 0.0376 mg of co-crystals **3**, **5** and **7** respectively in 10 mL of methanol such that all the solutions have unique concentration (1×10^{-5} M) with respect to the monomer **1P** as the initial % of the reaction is zero. In a similar way the UV-vis absorption was recorded at different stages of the reaction of **3**, **5** and **7** by exposing them to room

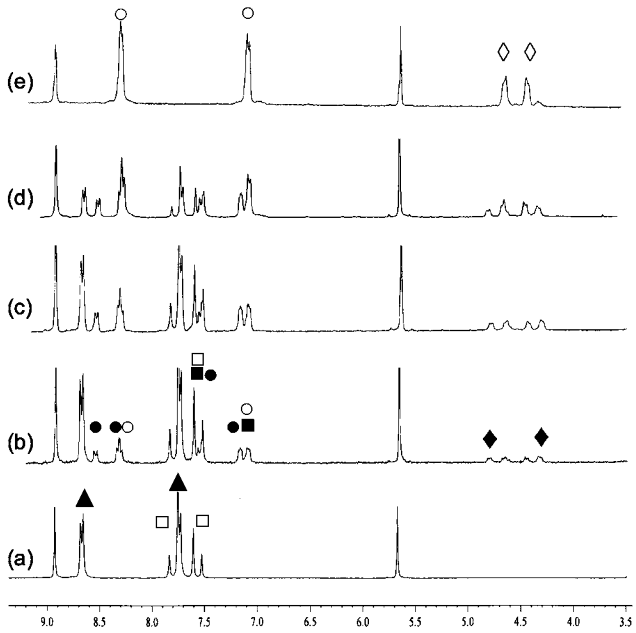


Fig. 8 ^{1}H NMR spectra in d^6 DMSO recorded at various stages of reaction in co-crystal **5**: (a) before irradiation; the gradual changes as the reaction progresses shown in (b) to (d); (e) after 100% reaction occurs: ▲ (Py–H of **1P**), ● (Py–H of MCB), ○ (Py–H of TCD), □ (alkene–H of **1P**), ■ (alkene–H of MCB), ◆ (cyclobutane–H of MCB), ◇ (cyclobutane–H of TCD).

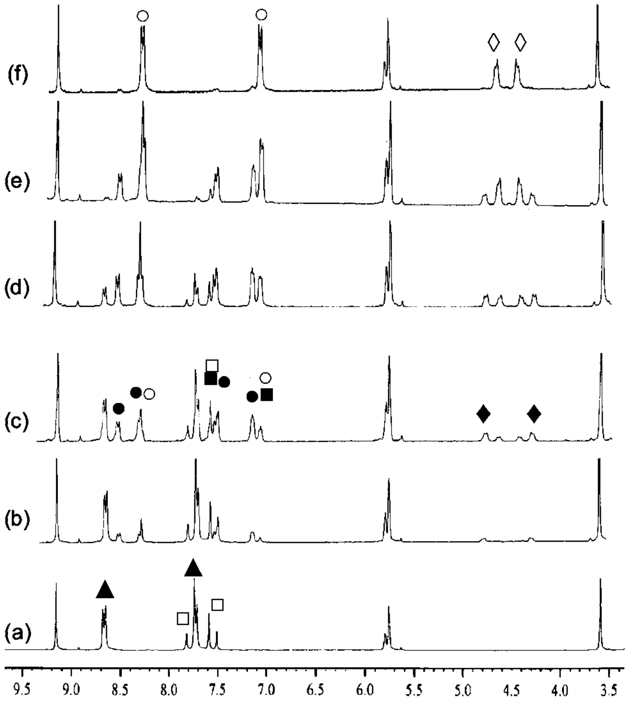


Fig. 9 ^{1}H NMR spectra in d^6 DMSO at various stages of the reaction in co-crystal **7**: (a) before irradiation; the gradual changes as the reaction progresses shown in (b) to (e); (f) after 100% reaction occurs: symbols represent various proton positions as mentioned in Fig. 8.

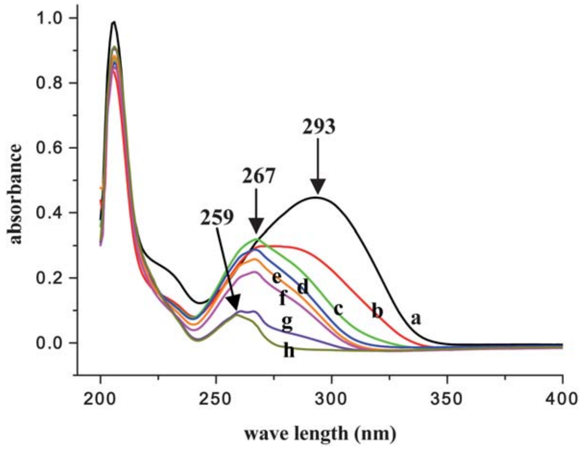


Fig. 10 UV-vis absorption spectra recorded for co-crystal **3** at various stages of the reaction. The curve (a) represents reactants and (h) represents products.

light. The initial spectrum of **3** (*i.e.* at 0% of reaction) exhibits absorption maxima (λ_{max}) at 206 nm (PG) and 293 nm (styryl pyridine) (Fig. 10). The UV-vis spectrum of the product with 100% TCD does not exhibit λ_{max} at 293 nm but exhibits new λ_{max} at 259 nm due to hypsochromic and hypochromic shifts. Initially (curves b and c) the molar absorptivity (ε) at the 267 nm increases and gradually decreases as the reaction progresses (curves c–i). Finally it disappears after the complete conversion of **1P** to TCD. These observations clearly indicate that the absorption maximum at 267 nm corresponds to the product MCB. The peak position and the molar absorptivity at 206 nm remain unaltered throughout the reaction as it corresponds to molecule PG. For the sake of comparison we have also measured the UV-vis spectrum for the product (**8**) obtained from the topochemical reaction of **1P** which has the similar chromophore as the MCB. The dimer **8** exhibits λ_{max} at 274 nm which is closer to that of MCB (267 nm). The UV-vis absorption for the other two reactive co-crystals **5** and **7** has also exhibited similar features as those observed for **3** (Fig. 11 and 12).

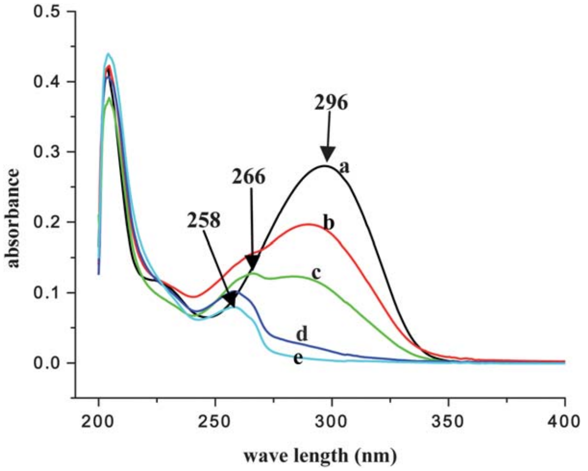


Fig. 11 UV-vis absorption spectra recorded for co-crystal **5** at various stages of the reaction. The curve (a) represents reactants and (e) represents products.

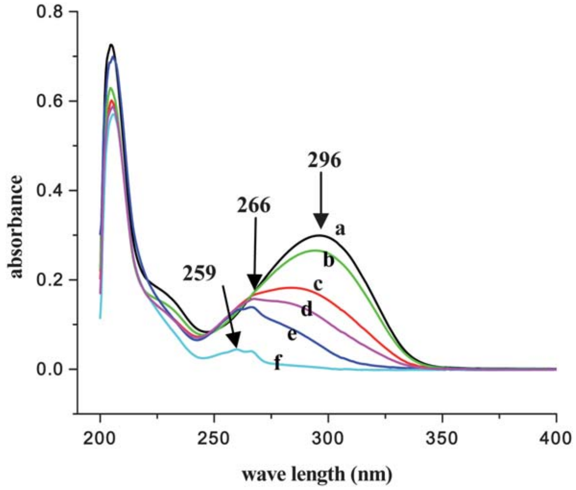


Fig. 12 UV-vis absorption spectra recorded for co-crystal **7** at various stages of the reaction. The curve (a) represents reactants and (f) represents products.

Photochemical reactions of the solvent free co-grounded solids of 1P with RN, PG and MR

In recent days mechanochemical grinding of two components was recognized as very efficient and environment friendly root to obtain materials which are chemically equivalent to the ones that are synthesized *via* co-crystallizing the components by conventional solvent evaporation.[19,20] We have analyzed the potentiality of the templates RN, PG and MR to form complexes with **1P** by mechanical grinding and compared the XRPD patterns of grounded samples with those of conventionally prepared

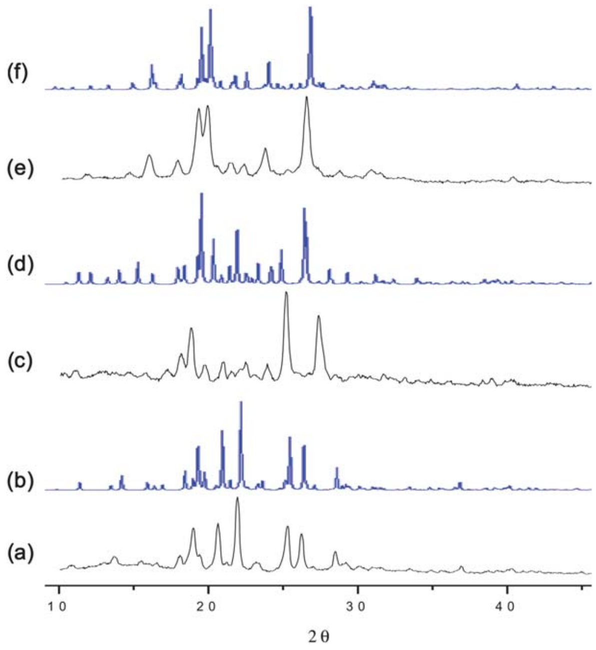


Fig. 13 XRPD patterns for co-grounded samples and respective co-crystals (calculated): (a) co-grounded sample of **1P** and RN; (b) co-crystal **2**; (c) co-grounded sample of **1P** and PG; (d) co-crystal **6**, and (e); co-grounded sample of **1P** and MR; (f) co-crystal **7**.

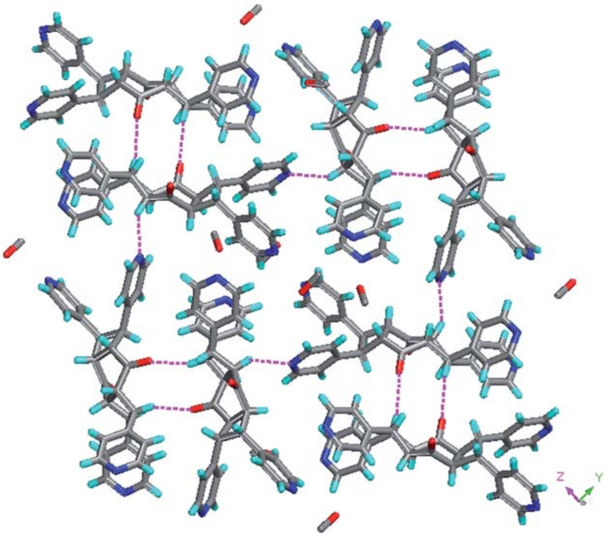


Fig. 14 Hydrogen bonded 2D layer in the crystal structure of **11**.

materials. It was found that the co-grinding of RN or MR with **1P** (in 1 : 1 ratio) produces the materials which are equivalent to **2** or **7** respectively (Fig. 13). The XRPD patterns of these co-grounded samples match totally with those of **2** and **7**. The photochemical reactivity of these samples also remains same as that of **2** and **7**, that is in the case of RN the co-grounded material is unreactive whereas in the case of MR the material is reactive with 100% yield of TCD. Further, the XRPD patterns of co-grounded samples of PG with **1P** do not match with those of **3**, **4**, **5** or **6**. Upon irradiation of this co-grounded solid resulted in the mixture of uncharacterized products. The difference in XRPD patterns and photochemical behavior from those of **3–6** indicates that the co-grounded sample PG and **1P** could be a new phase of co-crystalline material of the components.

Isolation of TCD

Finally the product TCD was isolated in almost quantitative yield from any of the 100% reacted co-crystals of **3–5** or **7** by acid–base work-up. Suitable single crystals of [TCD·2MeOH] (**11**) were grown by crystallizing the isolated TCD from methanol. Crystal structure analysis shows that the TCD is not as symmetrical as the one observed in **10** (Fig. 14). In the lattice two TCDs are paired *via* the C–H···O hydrogen bond synthons between carbonyl oxygen and cyclobutane C–H. These pairs are further connected into 2D sheets through herringbone type of arrangement involving C–H···N hydrogen bonds and methanol molecules remain hydrogen bonded to pyridyl nitrogens.

Conclusions

In conclusion we have demonstrated the synthesis of double [2 + 2] photodimerized product (TCD) from a new bis-pyridyl olefin (**1P**) in four co-crystal forms utilizing the hydrogen bonding interactions. Our studies also reveal that a quick and environmental friendly synthesis of the TCD is possible by a (1 : 1) mechanochemical grinding of **1P** and MR. The results presented here clearly support the stepwise mechanism for double [2 + 2] reaction of **1P**. Single crystal-to-single crystal conversion was observed only in one of the reactive forms. The lack of correspondence between geometry of reactants and the geometry of the product in **5** and the unreactivity in **6** despite satisfying the Schmidt's topochemical criteria are two anomalies observed in this paper. Although several examples with such anomalies are known the reasons are not so clear. The pedal motion was attributed for the observed difference in **5**, while the restricted molecular motion was attributed to the lack of reactivity in **6**. We note here that out of seven crystal structures containing **1P** four have the cisoid–cisoid conformation of **1P** while two have the cisoid–transoid conformation of **1P** and one has both conformations with 50% of occupancy each (disordered). Currently we are exploring coordination polymers of TCD and **8** with various metal salts.

Experimental

FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Powder XRD patterns were recorded with a PHILIPS Holland PW-1710 diffractometer. ^{1}H NMR and ^{13}C NMR (200/400 MHz) spectra were recorded on a BRUKER-AC 200/400 MHz spectrometer. UV-vis absorption was recorded using a Shimadzu UV-1601 spectrophotometer. Elemental analyses were carried out by a Perkin Elmer Series II 2400 and melting points were recorded using a Fisher Scientific melting point apparatus cat. No. 12-144-1.

Preparation of co-crystals **2–3**, the photochemical reaction details for **3** and generation of co-crystals **9–10** have been described in our previous communication. Co-grounded samples of **1P** with RN, PG or MR in 1 : 1 ratio were prepared by using mortar and pestle with about 1 hour continuous grinding.

Photochemical reaction of crystalline 1P and separation of product 8

Rod-like light yellow colored crystals of **1P** (4 g) were obtained by crystallization from toluene which were then exposed to sunlight for a day. A maximum conversion to the product **8** occurs at this stage of irradiation (as checked by ^{1}H NMR spectra and TLC) which otherwise go for polymerization on further irradiation. The partially irradiated material was then dissolved in methanol (15 mL) to produce a reddish color solution. A white solid gradually settles down from this solution which was then again recrystallized from methanol. The solid compound was characterized as the single [2 + 2] reaction product **8** (yield: 0.609 g, 15%). Mp 215–220 °C; (Found C, 76.73; H, 5.04; N, 11.51. Calc. for $C_{30}H_{24}N_4O_2$: C, 74.25; H, 5.12; N, 11.86%); λ_{max}(MeOH)/nm 203, 274; ν_{max}/cm^{-1} 3200, 1617, 1535, 1498, 1420, 1298, 1160, 1009, 815, 784, 732; δ_H(400 MHz; D$_6$-DMSO) 4.639/4.752 (AA'BB′, 4H, Cy-butane proton), 6.806 (d, *J* = 16.8 Hz, 2H, olefin proton); 7.370 (d, *J* = 6 Hz, 4H, Py–βH), 7.405 (d, *J* = 16.8 Hz, 2H, olefin proton); 7.528 (d, *J* = 6 Hz, 4H, Py–βH), 8.496 (d, *J* = 5.6 Hz, 4H, Py–αH), 8.593 (d, *J* = 6 Hz, 4H, Py–αH); δ_C(200 MHz; D$_6$-DMSO) 198.06 (2C, carbonyl); 150.85 (4C, vinyl Py C$^{2/6}$), 149.89 (4C, cyclobutyl Py C$^{2/6}$), 148.30 (2C, Cyclobutyl Py C^4), 141.97 (2C, vinyl Py C^4), 140.80 (2C, alkene C β to carbonyl), 130.15 (2C, alkene C α to carbonyl), 123.79 (4C, cyclobutyl Py C$^{3/5}$), 122.53 (4C, vinyl Py C$^{3/5}$), 49.70 (2C, cyclobutane).

Preparation of co-crystals 4

A 1 : 1 mixture of **1P** (0.05 g, 0.212 mmol) and PG $\cdot 2H_2O$ (0.0343 g) was dissolved in methanol (8 mL) and left at room temperature in the dark for slow evaporation. Light yellow colored block shaped crystals of **4** were obtained in 57% yield with respect to **1P** after 3–4 days. Single crystals completely loose water at 120 °C then started gradual blackening above 180 °C and no clear melting up to 300 °C; (Found C, 67.47; H, 5.04; N, 7.82. Calc. for $C_{78}H_{74}N_8O_{17}$: C, 67.13; H, 5.34; N, 8.03%); ν_{max}/cm^{-1} 3260, 3055, 2902, 2686, 1673, 1651, 1631, 1600, 1550, 1490, 1421, 1348, 1326, 1302, 1162, 1149, 1113, 1002, 984, 822, 692, 555; δ_H(200 MHz; D$_6$-DMSO) 5.635 (s, 9H, aromatic H of PG), 7.552/7.783 (AB quartet, 16H, alkene proton), 7.728 (d, J = 5.6 Hz, 16H, Py–βH), 8.667 (d, J = 5.6 Hz, 16H, Py–αH), 8.922 (s, 9H, PG–OH).

Preparation of co-crystal 5

A 1 : 1 mixture of **1P** (0.05 g, 0.212 mmol) and PG$\cdot 2H_2O$ (0.0343 g) was dissolved in acetonitrile (10 mL) and water (5 mL), and kept at room temperature in the dark for slow evaporation. Brownish rhombic shaped crystals of **5** were obtained in 85% yield with respect to **1P** after 2–3 days. The crystal of **5** found to loose water at around 120 °C and finally melts at 177–180 °C; (Found C, 68.11; H, 5.78; N, 8.56. Calc. for $C_{36}H_{38}N_4O_6$: C, 69.44; H, 6.15; N, 9.00%); λ_{max}(MeOH)/nm 204 and 296; ν_{max}/cm^{-1} 3202, 2626, 1662, 598, 1552, 1498, 1414, 1346, 1329, 1302, 1184, 1164, 1152, 1002, 984, 820, 563; δ_H(200 MHz; D$_6$DMSO) 5.637 (s, 3H, aromatic H of PG), 7.552/7.784 (AB quartet, 8H, alkene proton), 7.728 (d, J = 6 Hz, 8H, Py–βH), 8.667 (d, J = 6 Hz, 8H, Py–αH), 8.928 (s, 3H, PG–OH).

Preparation of co-crystal 6

A 1 : 1 mixture of **1P** (0.05 g, 0.212 mmol) and PG $\cdot 2H_2O$ (0.0343 g) was dissolved in toluene (10 mL) and methanol (5 mL) and left at room temperature in the dark for slow evaporation. Orange colored plate like crystals of **6** were obtained in 86% yield after 10–12 hours. The crystals started gradual blackening above 180 °C and no clear melting up to 300 °C; (Found C, 68.73; H, 4.84; N, 7.36%. Calc. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73); ν_{max}/cm^{-1} 3518, 3033, 2912, 2794, 2633, 1680, 1654, 1626, 1599, 1552, 1499, 1417, 1344, 1318, 1163, 1146, 1104, 1002, 985, 821, 689, 556; δ_H(400 MHz; D$_6$-DMSO) 5.633 (s, 3H, aromatic H of PG), 7.559/7.779 (AB quartet, 4H, alkene proton), 7.730 (d, J = 5.6 Hz, 4H, Py–βH), 8.668 (d, J = 5.6 Hz, 4H, Py–αH), 8.925 (s, 3H, PG–OH).

Preparation of co-crystal 7

A 1 : 1 mixture of **1P** (0.05 g, 0.212 mmol) and MR (0.0296 g) was dissolved in acetonitrile (10 mL) and methanol (2 mL) and left at room temperature in the dark. Light yellow colored block shaped crystals of **7** were obtained in 64% yield after 2–3 days. Mp: 180–182 °C; (Found C, 68.94; H, 5.01; N, 7.16. Calc. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44%); λ_{max}(MeOH)/nm 205 and 296; ν_{max}/cm^{-1} 3033–2580, 1684, 1662, 1630, 1601, 1552, 1499, 1441, 1419, 1382, 1343, 1320, 1210, 1187, 1171, 1154, 1104, 1090, 1005, 985, 838, 821, 554; δ_H(200 MHz; D$_6$DMSO) 3.594 (s, 3H, methoxy), 5.760 (d, J = 2 Hz, 2H, aromatic H of MR), 5.797 (d, J = 2 Hz, 1H, aromatic H of MR), 7.550/7.781 (AB quartet, 4H, alkene proton), 7.727 (d, J = 6 Hz, 4H, Py–βH), 8.666 (d, J = 6 Hz, 4H, Py–αH), 9.157 (s, 2H, MR–OH).

Separation of TCD from the reactive co-crystals 3–5 and 7

About 1 g of 100% photochemically reaction products in each case was dissolved in 50 mL water by adding HCl (1 N) dropwise (until all material dissolved). The solution was extracted with 50 mL ethyl acetate 3–4 times. The aqueous part was then neutralized by dropwise addition of dilute aqueous tri-ethylamine solution. The white precipitation obtained was filtered and washed with water and dried. The TCD obtained in almost quantitative yield. Mp 210–215 °C; (Found C, 75.07; H, 5.27; N, 11.15. Calc. for $C_{30}H_{24}N_4O_2$: C, 76.25; H, 5.12; N, 11.86%); λ_{max}(MeOH)/nm 202, 259; ν_{max}/cm^{-1} 3044, 2615, 1718, 1607, 1559, 1490, 1422, 1320, 1151, 1067, 1004, 857, 821, 688; δ_H(200 MHz; D$_6$-DMSO) 4.398 (d, J = 5.2 Hz, 4H, Cy–butane proton); 4.616 (d, J = 5.2 Hz, 4H, Cy–butane proton), 7.051 (d, J = 5.6 Hz, 8H, Py–βH), 8.263 (d, J = 5.6 Hz, 8H, Py–αH); δ_C(200 MHz; D$_6$-DMSO) 209.87 (2C, carbonyl), 149.67 (8C, Py C$^{2/6}$), 147.85 (4C, Py C^4), 123.68 (8C, Py C$^{3/5}$), 49.94 (4C, cyclobutane C α to carbonyl), 44.70 (4C, cyclobutane C β to carbonyl).

Crystal structure determination

All the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo Kα radiation (μ = 0.71073 Å) at room temperature (293 K) by hemisphere method. The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.[21] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The H-atoms attached to O-atom are located wherever is possible and refined using the ridging model. The single crystal data and refinement details for **1P**, **2**, **3**, **9**, **10** and **11** were communicated in our previous communication. Pertinent crystallographic (**4–8**) and hydrogen bonding parameters (**1P** and **2–11**) are given Tables 1 and 2 respectively. The **1P** molecules in **6** are disordered such that one of the double bond has both cisoid and transoid geometries with 50% occupancies. Due to this disorder two of the pyridine C-atoms and CO group of **1P** also exhibit two positions with 50% occupancy each (Fig. 15). The water molecule in **7** exhibits very high thermal motion indicating possible disorder or partial loss of water. Therefore platon squeeze option was used in the final refinement and corresponded with the removal of the contributions of 1/4 of a water molecule per asymmetric unit.[22]

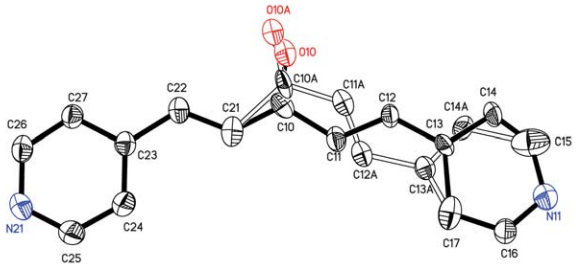


Fig. 15 ORTEP drawing of **1P** illustrating the disorder in **6**.

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