

REGULAR ARTICLE

Solid state photodimerization in an organic salt of 1,2-bis(4-pyridyl)ethylene and trifluoromethane sulphonic acid via pedal-like motion

ABDUL MALIK P PEEDIKAKKAL* 

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
E-mail: abdulmalik@kfupm.edu.sa

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Abstract. A novel organic salt, [bpeH].TFMS (**1**), of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) was synthesized using trifluoromethane sulphonic acid (CF₃SO₃H, TFMS) by self-assembly and its crystal structure was determined by X-ray crystallography. Compound **1** forms hydrogen-bonded assembly of [bpeH]⁺ cations and CF₃SO₃⁻ anions which are held together by N–H···N, C–H···O and C–H···F hydrogen-bonding interactions. An attempt has been made to orient the olefinic C=C bonds of bpe in the organic salt *via* weak hydrogen-bonding interaction for photodimerization reaction in the solid state. The [bpeH]⁺ cations are in parallel orientation in the infinite one dimensional (1D) chain through N–H···N hydrogen bonding. The olefinic C=C bonds of bpe are aligned in criss-cross orientation with a center-to-center distance of 4.97 Å. Even though the distance and the orientation of olefinic C=C bonds do not conform with the Schmidt topochemical criteria, compound **1** undergoes photodimerization reaction in solid state to produce stereo-specific *rcct*-tetrakis(4-pyridyl)cyclobutane (*rcct*-tpcb) (**2**) in 100% yield. The photoreactivity is expected to take place through cooperative movement of 1D chains and pedal-like motion of the pyridyl rings over the double bonds. The photodimerized product **2** undergoes acid-catalyzed isomerization to produce other cyclobutane isomers such as *rcct*-tpcb and *rtct*-tpcb. This strategy for synthesizing organic salts is a facile step for the synthesis of cyclobutane derivatives.

Keywords. Organic salts; 1, 2-bis(4-pyridyl)ethylene; photodimerization; pedal motion.

1. Introduction

Solid state photodimerizations have drawn considerable attention in crystal engineering due to their selectivity, high yield, solvent-free environmental friendliness and easy access to molecules that are otherwise inaccessible in solution.¹ The Schmidt topochemical postulates describe specific geometric criteria for such solid state photochemical reactions such as requiring parallel orientation of photoreactive double bonds with centroid distance between 3.5–4.2 Å.² The crystal engineering principles are effectively utilized to orient the C=C bonds of bpe (bpe = *trans*-1,2-bis(4-pyridyl)ethylene) in the solid state for photodimerization reactions.^{1c–d, 3–7} In this context, several organic co-crystals,^{3a,b} organic salts,⁴ discrete coordination complexes⁵ and coordination polymers^{1c–d, 3d–e, 6} (or metal-organic frameworks) have been studied for photodimerization in the solid state. Among the salts of bpe, chloride, trifluoroacetate (TFA) and 1,2,3,4-cyclobutane tetracarboxylate are effective for orienting the C=C bonds.⁴ The strength

of the hydrogen bond, including N–H···O and C–H···O and C–H···F, promotes the alignment of the olefinic C=C bonds in bpe.TFA.^{4a} Although the use of directional hydrogen bonding to bring two C=C bonds closer for photochemical reactions is well documented in organic salts, this strategy is rarely used in salts of bpe ligands containing C=C bonds.

While most solid state reactions follow the topochemical principle by maintaining the symmetry of monomers in the crystal lattice with small changes in dimension, some systems satisfying the Schmidt criterion did not undergo photodimerization.^{1a, 7} Such reactions that require large molecular motion of atoms in the solid state lattices are increasingly being discovered.^{8,9} Molecular motions are possible in crystals without disturbing surrounding molecules, especially intrinsic molecular movements including pedal-like motions, that lead to conformational changes in crystal lattice prior to dimerization.⁹ Molecular motion can be induced by external forces such as light irradiation or mechanical motion in the crystal lattice.¹⁰ The pedal-like motion is known to take place in numerous types of molecules, such as (E)-stilbenes, azobenzenes, N-benzylideneanilines

*For correspondence

and 1,2-diphenylethanes.⁹ The pedal-like motion was also reported in photodimerization and photoisomerization reactions.^{3d, 5e, 11} The pedal-like motion in crystals was also supported through theoretical calculations.¹² The presence of empty channels or large void volume in loosely packed crystals with normally weak hydrogen bonds can promote molecular motions in the solid state.¹³ The molecules can migrate easily if they are not interlocked inside the crystal packing. The pedal motion was also observed in hydrogen-bonded coordination complex systems containing bpe as the ligand.^{5e} This hydrogen-bonded coordination complex shows structural transformation induced *via* mechanochemical force which transformed its photoreactivity.

Tetrakis(4-pyridyl)cyclobutane (tpcb) can exist in four stereoisomers, namely *rcct* (*regio cis, trans, trans* relative to the first pyridyl group as a reference), *rtct*, *rcct* and *rccc*. This paper reports the synthesis and X-ray crystal structure of a novel organic salt, [bpeH].TFMS (**1**), of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) and trifluoromethane sulphonic acid (CF₃SO₃H, TFMS) and its photodimerization in the solid state. The photodimerized product undergoes isomerization reaction in solution and produces all the three isomers except *rccc*.

2. Experimental

2.1 Methods and materials

All chemicals were purchased from commercial sources and used as received. All solvents used were of reagent grade. UV irradiation was conducted by using Luzchem photoreactor (wavelength 350 nm, Intensity ~1.75 mW cm⁻²). The yields observed in UV irradiation experiments are reported in terms of the product distribution obtained by integrating the intensity of the isomers in ¹H NMR spectra. The NMR spectra were recorded with a Bruker ACF 300FT-NMR spectrometer with TMS as internal reference. FT-IR spectra were recorded from KBr pellets (FTS 165 Bio-Rad FT-IR).

2.2 Synthesis

Synthesis of [bpeH].TFMS (**1**): Triflic acid (0.50 mmol, 0.075 g) was added to a 4 mL methanolic solution of bpe (0.50 mmol, 0.091 g) and the mixture was stirred for 1 h in a round bottom flask. A white solid formed was filtered and dried under *vacuo*. [Yield: 0.14 g, 84%]. Elemental analysis: Calculated for C₂₆H₂₂N₄O₆S₂F₆ (664.6): C, 46.99; H, 3.34; N, 8.43; S, 9.65%. Found: C, 46.82; H, 3.35; N, 8.28; S, 9.62%. ¹H NMR (300 MHz, DMSO-*d*₆, 298 K, TMS): δ 8.59 (d, 4H, -pyridyl proton), 7.59 (d, 8H, -pyridyl proton), 7.52 (s, 4H, CH=CH) ppm. IR ν/cm⁻¹: 2464w, 2069w, 1608m, 1509w, 1405w, 1277s, 1222w, 1154m, 1027s, 977w, 832m, 629m, 551m, 516w.

The single crystals were obtained using the following method. 20 mg of **1** was dissolved in 4 mL of acetonitrile. The solution was then separated into two tubes by pipetting 2 mL of it into another test tube. Both tubes were placed in a bottle containing 10 mL of Et₂O. Long rod-like colorless crystals were formed after a week, which were separated under optical microscope for X-ray analysis.

2.3 UV irradiation

20 mg of solid powdered compound was packed between two Pyrex glass slides and was irradiated under UV irradiation for 24 h. UV irradiation experiments were completed by turning the packed glass slides for each sample half-way during irradiation to ensure uniform irradiation. ¹H NMR spectra were acquired to determine the percentage of dimer formed. The single crystals of **1** were not intact after UV irradiation. Pale yellow powder was collected after 24 h of UV irradiation. Irradiation of **1** after 24 h produces [rcct-tpcb(TFMS)₂] (**2**) in 100% yield. Elemental analysis: Calculated for C₂₆H₂₂N₄O₆S₂F₆ (664.6): C, 46.99; H, 3.34; N, 8.43; S, 9.65%. Found: C, 46.32; H, 3.33; N, 8.44; S, 9.68%. ¹H NMR (300 MHz, DMSO-*d*₆, 298 K, TMS): δ 8.44 (d, 4H, δ-pyridyl proton), 7.60 (d, 4H, δ-pyridyl proton), 5.07 (s, 4H, δ-cyclobutane proton) ppm. IR ν/cm⁻¹: 3096w, 2573w, 2172w, 1639m, 1609m, 1509s, 1420w, 1281s, 1259s, 1225m, 1165m, 1030s, 826m, 639m, 577w, 543m, 515w.

2.4 Isomerization

10 mg of irradiated compound **2** was dissolved in DMSO-*d*₆ (0.4 mL) and the isomerization reaction was monitored using ¹H NMR spectroscopy over a period of time (Figure S3 in Supplementary Information). The peaks for the protonated isomers *rcct*-tpcb, *rtct*-tpcb and *rcct*-tpcb were observed which confirm quantitative formation of *rtct*-tpcb and *rcct*-tpcb isomers in solution. Isomer *rtct*-tpcb predominates as the major product after 30 min heating at 100°C (Figure S4 in Supplementary Information). The product distribution (%) of isomers was calculated based on the integrated intensity of ¹H NMR signals for each isomer. ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ 8.92 (d, 2H, Py-H for *rcct*-tpcb), 8.85 (d, 8H, Py-H for *rtct*-tpcb), 8.68 (d, 12H, Py-H for *rcct*-tpcb and *rcct*-tpcb), 8.46 (d, 2H, Py-H for *rcct*-tpcb), 8.24 (d, 2H, Py-H for *rcct*-tpcb), 7.97 (d, 8H, Py-H for *rtct*-tpcb), 7.79 (d, 4H, Py-H for *rcct*-tpcb), 7.71 (d, 4H, Py-H for *rcct*-tpcb), 7.46 (d, 4H, Py-H for *rcct*-tpcb), 5.67 (m, 1H, CH-CH for *rcct*-tpcb), 5.20 (s, 4H, CH-CH for *rcct*-tpcb), 5.06 (m, 3H, CH-CH for *rcct*-tpcb), 4.46 (s, 4H, CH-CH for *rtct*-tpcb) ppm.

3. Results and Discussion

3.1 Trifluoromethanesulphonate salts of bpe

White solid product of **1** was obtained by adding TFMS to a methanolic solution of bpe in equimolar ratio.

Colorless rod-shaped crystals were obtained by slow diffusion of methanolic solution of the white product with diethyl ether. The single crystal for X-ray structural analysis shows that compound **1** crystallizes in the triclinic space group P-1 with $Z=2$. The asymmetric unit content is shown in Figure 1. The X-ray structure reveals an infinite chain hydrogen bonded assembly of $[\text{bpeH}]^+$ cations and CF_3SO_3^- anions held together by $\text{N-H}\cdots\text{N}$ interactions [$\text{N1-H1}\cdots\text{N2}$, 2.714(2), $\text{N3-H3}\cdots\text{N4}$, 2.718(2)], and further held by very weak $\text{C-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{F}$ interactions forming 1D linear chains of $[\text{bpeH}]^+$ cations, as shown in Figures 2 and 3. The self-assembly of olefins *via* $\text{C-H}\cdots\text{F}$ interactions using fluorinated reagents are known.¹⁴ The adjacent independent 1D linear chains, namely **A** \cdots **B**, run along the *b* direction. As a result, the $[\text{bpeH}]^+$

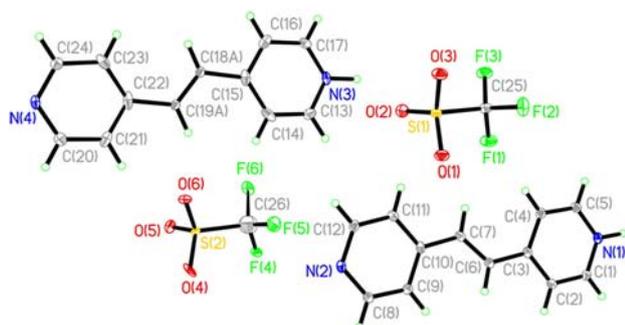


Figure 1. A view of the asymmetric unit content in **1**.

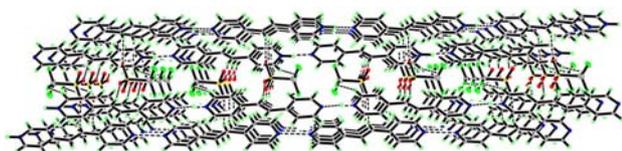


Figure 2. A view of the crystallographic packing of **1** along *b* direction.

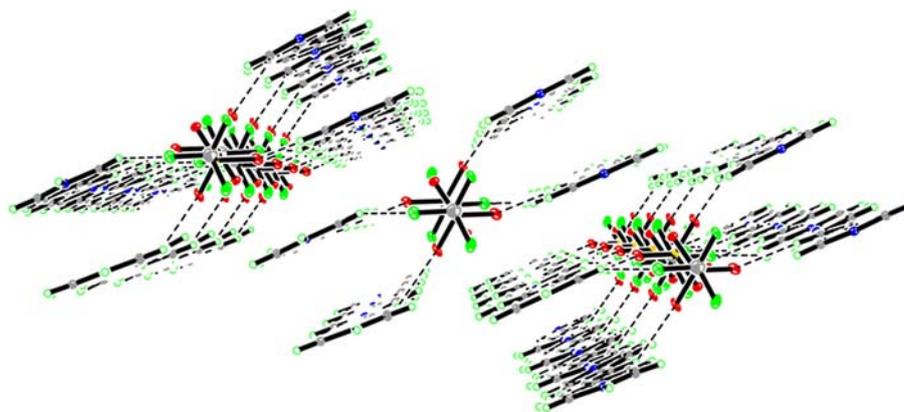


Figure 3. A view of the crystallographic packing of **1** showing $[\text{bpeH}]^+$ cations assembled in parallel through $\text{N-H}\cdots\text{N}$ interactions.

molecules are assembled in parallel orientation. However, the $\text{C}=\text{C}$ bond of $[\text{bpeH}]^+$ molecule is aligned in slip-stacked criss-cross orientation at a centroid distance of 4.97 Å, but in offset-stacked arrangement along *bc* plane, as shown in Figure 4. The structure does not fulfill the Schmidt's criteria^{2a} of $\text{C}=\text{C}$ bonds; however, the compound does undergo photochemical $[2+2]$ cycloaddition to form cyclobutane derivatives.

3.2 Photodimerization reaction

The protonated bpe molecules form hydrogen bonds with TFMS anions which is utilized as strategy to direct the alignment of the $\text{C}=\text{C}$ olefinic bonds. However, the crystal structure indicates that olefinic $\text{C}=\text{C}$ bonds do not satisfy Schmidt's criteria and hence they are predicted to be photostable. However, compound **1** was found to be photoreactive. When the crystals of **1** were irradiated for a period of 13 h, 100% conversion was observed and the crystals turned into pale yellow solid corresponding to 100% of $[\text{rctt-tpcb}(\text{TFMS})_2]$ (**2**). The ^1H NMR spectrum of the product **2** dissolved in $\text{DMSO-}d_6$ showed the complete disappearance of the olefinic protons at 7.52 ppm, and appearance of the protons of cyclobutane at 5.07 ppm, and corresponding shifts in the bipyridyl protons from 8.59 and 7.59 ppm to 8.44

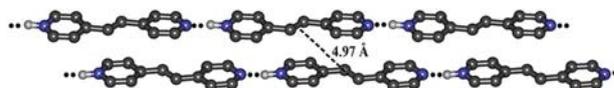
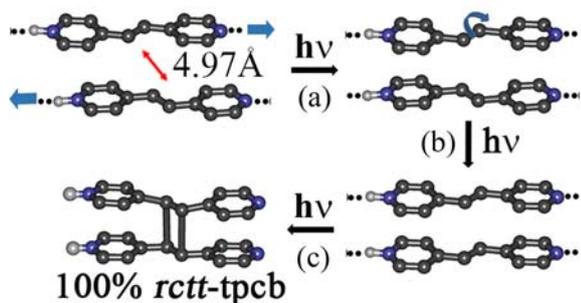
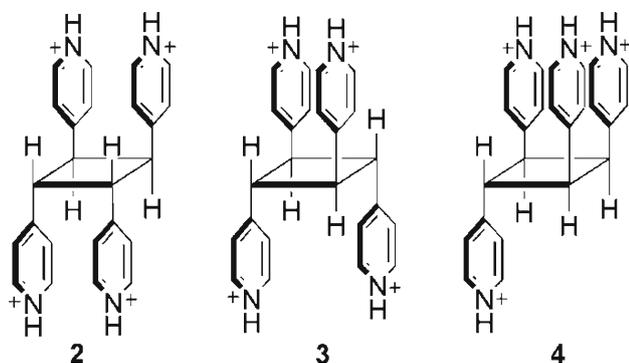


Figure 4. A view of the packing of adjacent independent infinite 1D hydrogen bonded assembly of $[\text{bpeH}]^+$ cations in the *bc*-plane. The C-H hydrogen atoms are omitted for clarity. The $\text{C}=\text{C}$ bonds are oriented in criss-cross orientation and the center-to-center distance between the olefinic $\text{C}=\text{C}$ bonds is 4.97 Å.



Scheme 1. Photodimerization pathway of **1**. (a) Molecular movement of 1D hydrogen bonded adjacent chain; (b) pedal like motion over the C=C double bonds; (c) parallel orientation of C=C bonds and the formation of 100% *rctt*-tpcb photodimer.



Scheme 2. The protonated *rctt*-tpcb (**2**), *rtct*-tpcb (**3**) and *rcct*-tpcb (**4**) isomers.

and 7.60 ppm. The quantitative photoreactivity of the crystals of **1** was quite unexpected based on the crystal packing. The olefinic C=C bonds of bpe are aligned in criss-cross orientation in **1** with a center-to-center distance of 4.97 Å. The olefinic C=C bonds of **1** need molecular motion to change the double bonds from criss-cross to parallel orientation for photoreactivity. The latter is expected to take place through cooperative movement of 1D chains and pedal-like motion of the pyridyl rings over the double bonds that make it possible to orient of C=C bonds from criss-cross to parallel orientation. The pyridyl ring in [bpe-H]⁺ can be freely rotated over the C=C olefinic bonds or pedal-like motion over the double bonds prior to dimerization as shown in Scheme 1. Such, intrinsic molecular movements, including pedal-like motion, were reported earlier for trans-stilbene and bpe respectively.^{5,9d} The photolysis of crystals of **1** was conducted in the solution state. The photoreactivity in DMSO-*d*₆ showed the formation of mixture of products including isomerized and dimerized [bpe-H]⁺, without selectivity as observed by ¹H NMR spectrum (Figures S5 and S6 in Supplementary Information).

3.3 Isomerization reaction

The acid-catalyzed isomerization of *rctt*-tpcb to *rtct*-tpcb and isomerization of *rctt*-HH-4,4-BPCD and *rctt*-HT-4,4-BPCD to their corresponding *rcct* isomers have been reported.^{4,5d,15,16} A very similar acid-catalyzed isomerization reaction was observed for **2** in DMSO-*d*₆. Scheme 2 shows the observed isomers in acid-catalyzed isomerization reaction. The chemical shifts are consistent with the stereochemistry of the cyclobutane rings and assigned by comparison of the ¹H NMR spectra with those reported for the dimers of 4, 4'-tpcb.⁴ The cyclobutane protons of *rtct*-tpcb have chemical shift values of about 0.74 ppm lower than the corresponding *rctt*-tpcb isomer at 4.45 ppm for the *rtct*-tpcb and 5.20 ppm for the *rctt*-tpcb cyclobutane protons in **2**, which are consistent with previous studies.⁴ An upfield shift for cyclobutane protons has been found for both *rctt*-tpcb and *rtct*-tpcb at about 5.20 and 4.45 ppm from **2**. A mutual magnetic anisotropic influence of pyridyl ring in *cis* position of *rctt*-tpcb brings up the pyridyl protons at the upfield position in comparison to *rtct*-tpcb. In the case of *rcct*-tpcb obtained from **2**, there are 6 sets of doublets from the pyridyl protons observed at 8.92 to 7.46 ppm and three sets (three triplets or one triplet and a multiplet) from the cyclobutane protons of **2** observed at about 5.67 (triplet for 1H), 5.06 (multiplet for 3H), as observed before.^{4,5d} The mechanism involved in the formation of tpcb type cyclobutane derivatives has been well described by Horner and Hünig.¹⁶ Initially, the isomerization reaction was monitored in DMSO-*d*₆ for a period of time at room temperature. Later, the isomerization reaction was observed to be faster upon heating at 100°C. The photodimerized product **2** produces 100% *rtct*-tpcb in DMSO-*d*₆, upon reflux for 30 min. This synthetic method reveals an easy way of producing stereospecific *rtct*-tpcb by heating which is otherwise photochemically inaccessible in the solid state. The tetrahedrally disposed pyridyl groups in *rtct*-tpcb displayed the ability of forming metal-organic frameworks with interesting topologies.^{4a}

4. Conclusions

In conclusion, a salt of bpe obtained by reaction with trifluoromethane sulfonic acid was investigated for its photoreactivity. The compound was expected to be photostable based on the crystal packing due to non-satisfaction of Schmidt's criteria; because, the olefinic C=C bonds of [bpe-H]⁺ molecules are aligned in slip-stacked criss-cross orientation at a centroid distance of 4.97 Å and in offset-stacked arrangement.

However, the compound was found to be photoreactive. The bpe ligands undergo quantitative conversion to produce cyclobutane derivative exclusively in *rcct* stereochemistry upon UV irradiation. This is again an exceptional case in which the olefinic bond does not need to be parallel under the Schmidt criterion to undergo photodimerization. The bpe ligands with antiparallel or criss-cross C=C bonds undergo pedal-like motion prior to photodimerization. Finally, the photodimerized product undergoes acid catalyzed reaction, as observed before in cyclobutane derivatives. Although the predictability of aligning C=C bonds is a challenge, the synthetic strategy of these salts using fluorinated inorganic acid plays a crucial role for the templated photoreaction. The synthesis of cyclobutane derivatives using photoreaction provides better understanding of the supramolecular interaction for covalent synthesis and intrinsic molecular movements in solids. Indeed, the acid-catalyzed isomerization reaction of *rcct*-tpcb provides an easy way of producing stereospecific *rtct*-tpcb which is otherwise photochemically inaccessible in the solid state.

Supplementary Information (SI)

CCDC 1504243 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or by e-mail to deposit@ccdc.cam.ac.uk. Supplementary information associated including NMR spectra, Thermal analysis, X-ray crystallographic analysis is available at www.ias.ac.in/chemsci.

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