



Isomerization of cyclobutane ligands in the solid state and solution

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ABSTRACT

Cyclobutane compounds are a class of compounds that can be conveniently synthesized in the solid state by employing crystal engineering principles. The *rcct*-isomer (or the *syn*-dimer) is the most common form of any cyclobutene compound that is obtained in the solid state by the photochemical [2 + 2] cycloaddition reactions. However, these *rcct*-isomers can be converted to other less accessible forms, under some special conditions. Isomerization of cyclobutane compounds thus plays an important role in synthetic chemistry. Such isomerization of cyclobutane compounds have been reported in organic salts, metal complexes, coordination polymers and metal-organic frameworks. In this review, these fascinating examples of isomerization that occur both in the solid state and solution phase have been discussed.

1. Introduction

Cyclobutane is a strained four-membered ring. Their derivatives are usually synthesized in solution by intramolecular [2 + 2] cycloaddition reaction. However, intermolecular cycloaddition is very messy in solution and result in several unwanted products. Recently progress has been made to obtain clean photoproducts using catalysts in solution [1–3]. On the contrary, solid-state [2 + 2] cycloaddition reactions are consistently used for intermolecular routes from a pair of alkenes containing organic molecules. The ground-breaking pioneering research work on solid-state [2 + 2] photochemical reactions of substituted *trans*-cinnamic acids and related alkene derivatives by Schmidt and co-workers in 1960's laid the foundations of solid-state organic photochemistry and crystal engineering [4,5]. Weak supramolecular interactions responsible for bringing a pair of alkenes have been successfully designed and exploited not only in the organic solids, but also metal complexes, coordination polymers (CPs) and metal-organic frameworks (MOFs) [6–17].

Of these, *trans*-1,2-bis(4'-pyridyl) ethylene (bpe) is one of the popular alkenes [7,8,11,16]. This is used as a model organic molecule to understand the way to pack the molecules in the solid state using different crystal engineering tools to satisfy the Schmidt's criteria for the solid-state [2 + 2] cycloaddition reaction, namely, the parallel orientations of the alkene bonds, and the distance between them to be less than 4.2 Å to allow for the overlapping of *p_z* orbitals [4–10]. Such an arrangement led to the formation of one of the four isomers of the

resultant photoproduct, namely, *regio cis*, *trans*, *trans*-(relative to the first pyridyl group as reference) tetrakis(4-pyridyl)cyclobutane (*rcct*-tpcb). All the isomers of the tpcb ligand, *rcct*, *rtct*, *rttt* (or *rcct*) and *rtcc*, are shown in Fig. 1. Almost all the solid-state [2 + 2] photochemical cycloadditions of bpe yielded exclusively the *rcct*-isomer. In contrast, reports on the formation of the most thermodynamically stable *rtct* isomer by the solid-state [2 + 2] cycloaddition reaction are rare which can only be obtained from the cyclization of the crisscrossed alignment of alkene pairs. Usually, the alkene bonds undergo pedal motion to rearrange themselves to parallel orientation before the photoreaction under UV light, as it required very little energy [18,19]. Of these isomers, except *regio cis*, *cis*, *cis* (*rtcc*) isomer, which is energetically not favorable, all the other three isomers (*i.e.*, *rcct*-, *rtct*-, *rcct*- or *rttt*-) have been obtained and used as ligands in making CPs and MOFs [20].

Solid-state [2 + 2] photocycloaddition reactions yielded several interesting *rcct*-cyclobutane derivatives. Isomerization of some of these cyclobutane derivatives have been investigated. Several of these isomers can be used as potential ligands for making CPs and MOFs. With this in mind, we reviewed isomerization of *rcct* isomers in the solid state and solution of several cyclobutane derivatives that have been obtained by photoreactions in our laboratory and by others.

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2. Solid-state and solution isomerization of *rtct*-tpcb and other derivatives

The DFT calculations (M06-2X/6-311 + G**//M06-2X/6-31G*) showed that the *rtct*-*tetrakis*(4-pyridyl)cyclobutane isomer is the more stable isomer, than *rtct*, *rttt* (or *rcct*) and *rtcc* isomers which have 15, 14 and 59 kJ mol⁻¹ respectively, higher in energy [21]. From these calculations it may be possible that the *rtct* isomer can be isomerized to *rtct* and *rttt* isomers but not to *rtcc* isomer.

The *rtct*-tpcb has been synthesized stereo-selectively by heating the solid *rtct*-tpcb at 190 °C for 12 h in air [21]. Detailed investigation showed that such a rare solid-state isomerization process occurred through a topochemical unimolecular mechanism by a radical chain pathway, initiated by molecular oxygen. This was further established by the formation of different products in the presence of oxygen and nitrogen, as confirmed by the detection of a radical intermediate in ESR study, as well as ESI-MS crossover experiments. The QM/MM and docking calculations showed that the isomerization occurs by topochemical control by the crystal lattice. Lattice strain, accumulated in the crystal after isomerization, possibly led to amorphization and recrystallization, as was observed in the PXRD experiments. It should be noted here that the solution-route isomerization of *rtct*-tpcb to *rtct*-tpcb happened through *rcct*-isomer as the intermediate (*vide infra*), while in the solid state, this isomerization happened in a single step.

The isomerization of *rtct*-tpcb was investigated in DMF-*d*₇ and DMSO-*d*₆ solution at 200 °C. The percentage of different isomers formed as monitored by ¹H-NMR spectroscopy was plotted with time, as shown in Fig. 2, revealed that no pure isomer was formed in solution.

3. Isomerization of salts of *rtct*-tpcb and other derivatives in solution

A simple route to synthesize the *rtct*-tpcb was described from the salt [bpeH₂](TFA)₂. When the powdered sample of this salt was irradiated under UV light for 24 h, [rtct-tpcb-H₄](TFA)₄ was obtained quantitatively. This can be converted to the corresponding *rtct*-isomer by heating the DMSO-*d*₆ solution of *rtct*-salt at 100 °C for 30 min. At lower temperatures *rcct*-isomer was also observed along with *rtct*- and *rttt*-isomers (Fig. 3) [22]. Salts of trifluoromethane sulfonic acid and sulfuric acid can also be used for this purpose [23,24].

Trans-3-(*n*'-pyridyl)acrylic acid (*n* = 2, 3, 4), a series of unsymmetric olefins, were converted into salts with various common acids, viz., HCl, H₂SO₄, CF₃CO₂H, HBF₄, HClO₄ etc, by protonating the pyridyl-*N* atom. The resulting salts were investigated for solid state photoreactivity.

Elucidation of crystal structures revealed that the unsymmetric olefin were stacked either in *head-to-head* (HH) or in *head-to-tail* (HT) parallel orientations, depending on the counter anions [25–27]. Thus, for each olefin, the *rtct*-form of two regio-isomers of the photodimers was obtained. Both the HH- and HT-dimers of 2-pyridyl (*i.e.* *ortho*-) and 4-pyridyl (*i.e.* *para*-) substituted compounds, namely, *rtct*-HT-2,2'-BPCD, *rtct*-HH-4,4'-BPCD, *rtct*-HT-4,4'-BPCD, (where BPCD = bis(*n*'-pyridyl) cyclobutane-*x,y*-dicarboxylic acid, (*x,y* = 1,3 or 2,4)) exhibited isomerization to the corresponding *rcct*-isomers (Fig. 4), when heated in the presence of acid. However, under similar condition, the 3-pyridyl (*i.e.*, *meta*-) substituted compounds, namely, *rtct*-HT-3,3'-BPCD, and *rtct*-HH-3,3'-BPCD did not show any isomerization (Fig. 4). Another distinct feature of isomerization in this series of compounds is that *rtct*-isomers can transform only to the *rcct*-isomers, no *rtct*-isomers were detected. This is because of non-participation of the carboxylic acid groups in this isomerization and flipping of only one pyridyl group was possible [28]. Similar observation was also noted with another bis (4'-pyridyl) substituted cyclobutane compound, confirming the wide applicability of the hypothesis [27].

4. Isomerization of cyclobutane compounds under hydrothermal conditions

Lang et al. demonstrated that one dimensional coordination polymer of *rtct*-tpcb can be converted to three-dimensional coordination polymer of *rtct*-tpcb under hydrothermal condition in the presence of an acid. [Cd(*rtct*-tpcb)_{0.5}(CBA)₂]_n (where HCBA = 4-chlorobenzoic acid) was obtained in photochemical single-crystal-to-single-crystal route as one dimensional polymer, which upon further treatment with HCl under hydrothermal conditions, converted to [Cd(*rtct*-tpcb)Cl₂].2H₂O having three-dimensional network. Herein, the *rtct*-tpcb underwent isomerization to *rtct*-tpcb in the process. In can be noted that the CBA ligand was lost from the coordination sphere during this transformation (Fig. 5) [29].

Briceño et al. have investigated the isomerization of dimers of bpe, 2,2'-bpe, and 2,4'-bpe in the presence of Mn(II), Al(III) under solvo/hydrothermal conditions [30]. Their dimers were obtained via photochemical route, and thereafter the *rtct*- and *rcct*-isomers were obtained under hydrothermal heating of the dimers in the presence of Lewis or Brønsted acids. When the dimers were refluxed, a mixture of *rtct*- and *rcct*-isomers were obtained; however, under hydro-/solvothermal condition the *rtct*-isomers were obtained in 100% yield. 1,2,4,5-benzenetetracarboxylic acid (bta) was used as the template to obtain *rtct*-form of the corresponding dimers, which after photodimerization was further

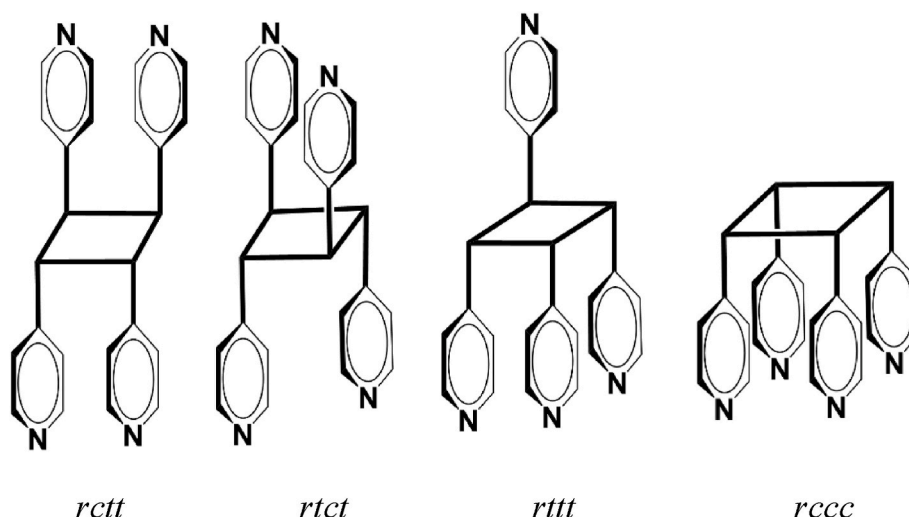


Fig. 1. Four regio-isomers of *tetrakis*(4-pyridyl)cyclobutane (tpcb).

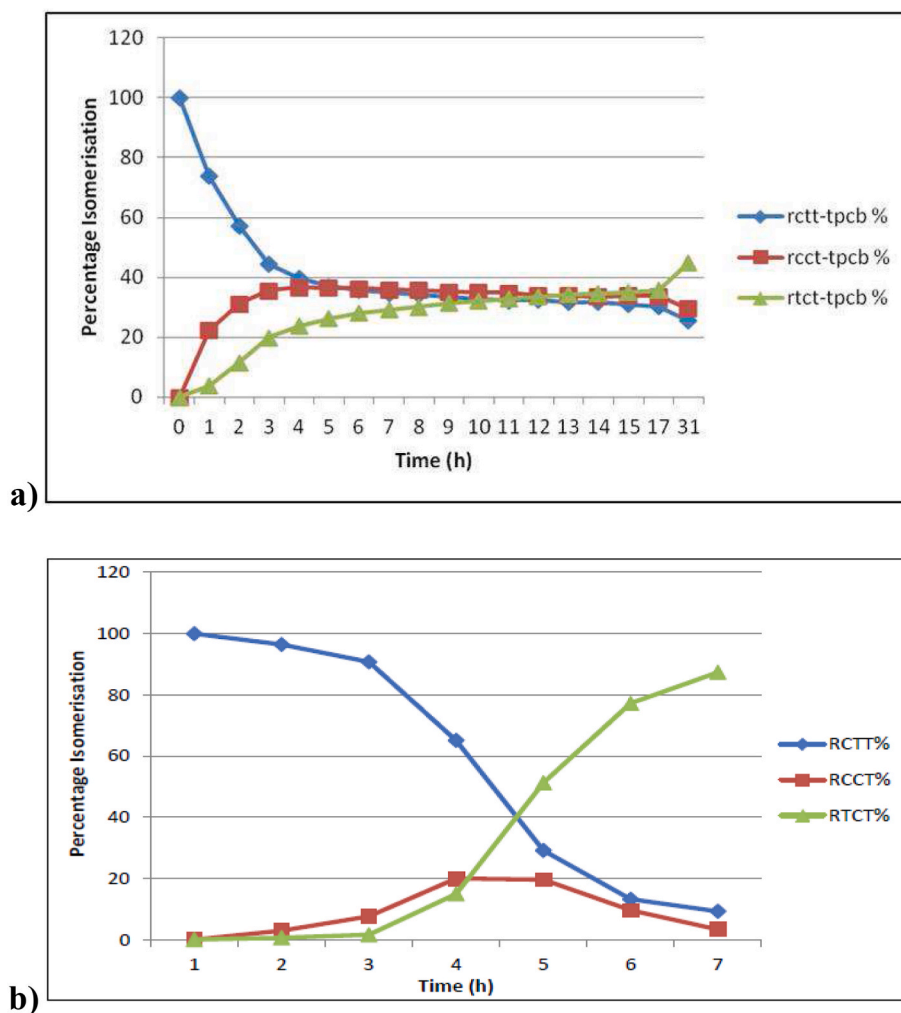


Fig. 2. The percentage versus time plot of the products obtained by heating a) *rctt*-tpcb in DMF-*d*₇ at 200 °C and b) in DMSO-*d*₆ at 200 °C. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (Ref. 21).

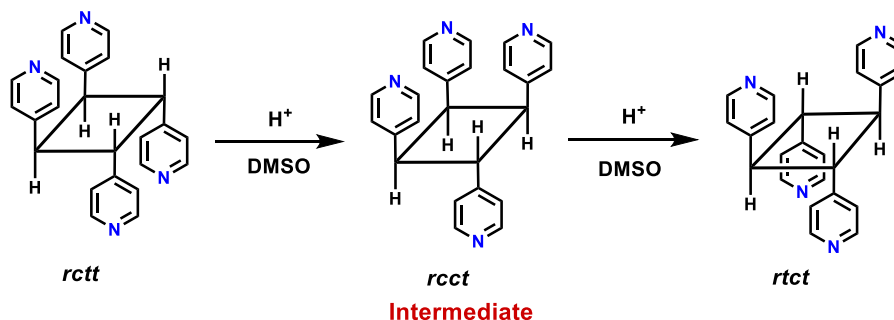


Fig. 3. Isomerization of the *rctt*-tpcb to *rtct*-tpcb goes through the *rcct*-isomer as intermediate, in the acidic medium.

heated to obtain the *rtct*-isomers quantitatively and were confirmed by X-ray crystallography. However, in case of 4-chlorostyrylpyridine (4-Cl-SP), only the *rcct*-isomer, and not the *rtct*-isomer of the dimer was observed. Both the *rtct*-4,4'-tpcb and *rtct*-2,4'-tpcb were found to be protonated, while *rcct*-4-Cl-dpcb, dimer of 4-Cl-SP was not protonated, as was revealed from the crystal structures of their salts with bta, obtained after recrystallization (Fig. 6) [30].

The *rtct*-form of these tetrapyrrolyl cyclobutane compounds, namely *rtct*-2,2'-tpcb, *rtct*-4,4'-tpcb, and *rtct*-2,4'-tpcb were further treated under hydrothermal conditions in the presence of ammonium polymolybdate.

It was observed that the *rctt*-isomers isomerized to the corresponding *rtct*-forms in all these cases, as were characterized by X-ray crystallography (Fig. 7) [31] (see Fig. 8).

5. Formation and synthesis of CPs and MOFs containing less-common isomers

The most commonly obtained *rctt*-isomer of cyclobutane compounds have been employed for constructing coordination polymers and metal organic frameworks. CPs or MOFs with *rctt*-form are mostly

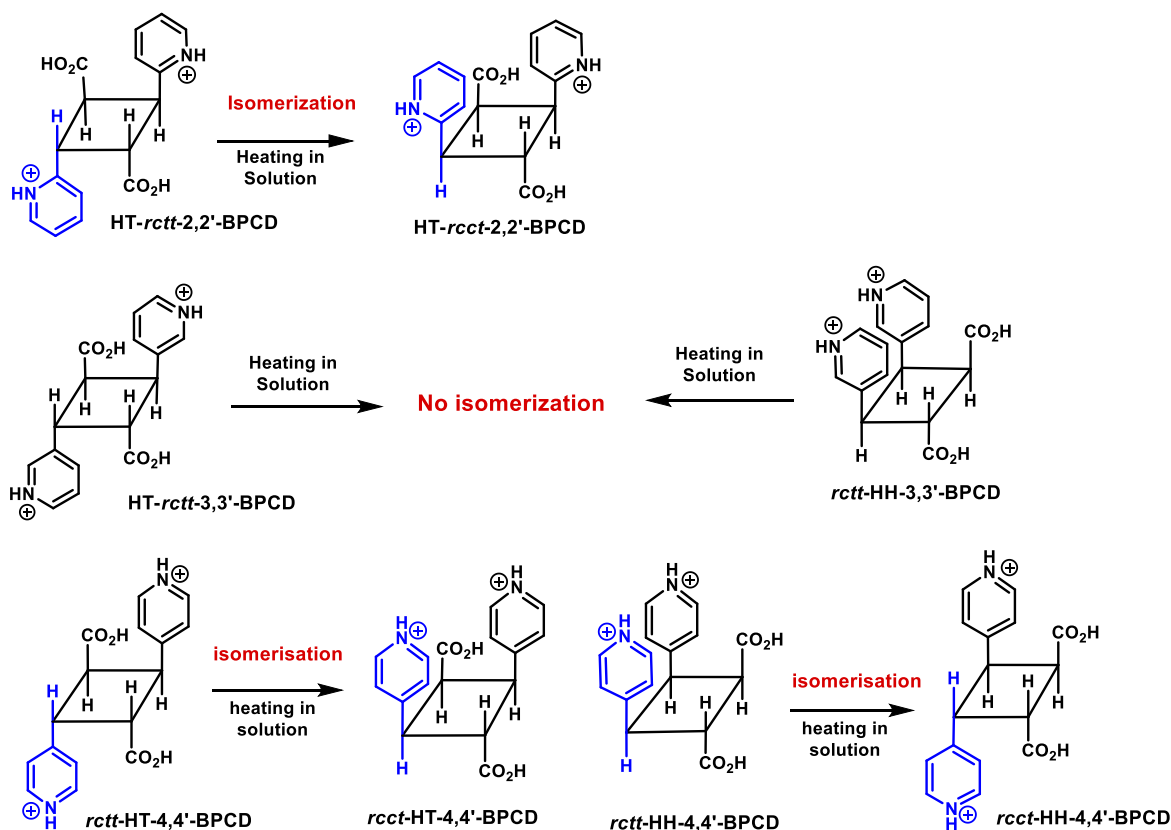


Fig. 4. Isomerization event in bis-(*n'*-pyridyl) substituted ($n = 2, 3, 4$) cyclobutane. Only *ortho*- and *para*-pyridyl compounds show isomerization, while *meta*-compounds not.

characterized with products obtained in *single-crystal-to-single-crystal* transformation, or from the recrystallization of the UV-irradiated debris. In some cases, the cyclobutane compounds have been isolated as pure compounds, characterized, and employed for the synthesis of CPs/MOFs. For example, *rcct*-tpcb was isolated and employed as tetratopic square planar building unit for the construction of two-dimensional (4,4) connected coordination polymer network with paddlewheel SBU [32]. Compound *rcct*-2,4'-tpcb was also employed to construct metal organic polyhedron with a transition-metal that hosted anions as guests [33]. Similarly, carboxylic acid functionalized cyclobutane compound, 1,2,3,4-tetrakis-(4'-carboxyphenyl) cyclobutane (*rcct*-H₄TCCB) was isolated as pure compounds and utilized as a potential building block for MOFs, as well as employed in the designed synthesis of cocrystals of intriguing topologies with dipyriddy spacers [34,35].

When bpe ligand was used for synthesis at room temperature, occasionally CPs and MOFs containing dimerized photoproduct, *rcct*-tpcb were obtained [36,37]. For example, the reaction of bpe with AgBF₄ in CH₃CN and CH₂Cl₂ in presence of light yielded a non-interpenetrating MOF [Ag(*rcct*-tpcb)](BF₄) with diamond (**dia**) topology [37]. However, when solvothermal/reflux conditions were used, isomerization occurs to produce the MOFs containing more stable *rtct*-tpcb [29,38].

Quantitative thermal isomerization of *rcct* isomer to *rtct*-isomers occurs cleanly when the solids of the two supramolecular isomers of [Na₂(*rcct*-cbtc-H₂)(H₂O)₄] and [K₂(*rcct*-cbtc)(H₂O)₂] were heated to 200 °C in air but not in solution [39]. For example, the ¹H-NMR spectroscopy of the solid obtained after heating [Na₂(*rcct*-cbtc-H₂)(H₂O)₄] was heated at 230 °C for 72 h in air and dissolved in D₂O, provided 85% of the *rtct*-isomer from the chemical shift at 3.13 ppm, in addition to the peak at 3.4 ppm due to C-H proton of the *rtct*-isomer. Recrystallization from water yielded [Na₃(*rtct*-cbtc-H₂)(*rtct*-cbtc-H₃)(H₂O)₃]. Similar isomerization was suspected to happen in the hydrothermal synthesis of Zn(II) MOFs [40].

As discussed before, when crisscrossed pairs of bpe undergo cyclization, they usually undergo pedal motion to parallel orientation to yield *rcct*-tpcb [18,19]. One such example is the photoreactions of a Zn (II) complex [Zn(bpe)₂(H₂O)₄](NO₃)₂·8/3H₂O·2/3bpe. In the solid state, a hydrogen-bonded aggregate was formed between the [Zn(bpe)₂(H₂O)₄]²⁺ complexes (Fig. 8). The adjacent bpe pairs are packed closely in a 'face-to-face' manner by the O-H...N hydrogen bonds. However, two-thirds of these alkene bond pairs are crisscrossed and hence these single crystals undergo partial conversion of bpe (46%) to the cyclobutene derivative in 25 h. Of these *rcct*-tpcb and *rtct*-tpcb are 39% and 7% respectively as monitored by ¹H-NMR spectroscopy. From these, it is understood that only partial pedal motion occurs. Upon grinding the single crystals to powder for 5 min using pestle and mortar, and irradiated under UV light for 25 h, 100% conversion is achieved which include the guest bpe in the anionic layer. Of these 13.4% are due to *rtct*-isomer. It is shown that the grinding triggered the pedal motion of the crisscrossed bpe pairs to align parallel, as well as the movements of the guest bpe molecules which are separated by 7.12 Å in the anionic layer closer to form both *rcct*- and *rtct*-isomers in equal amounts. Such behavior is akin to solution-like behavior where the dimerization is statistically expected to produce equal amounts of *rtct*- and *rcct*-isomers [41].

In some other occasions, MOFs containing *rcct*-isomers were also observed [42]. A neutral photoreactive zwitterionic Pb(II) complex, [Pb(TFA)₄(bpe-H)₂] (TFA = trifluoroacetate) yielded a photoproduct in powder form upon UV irradiation. The formation of a 1D CP [Pb(TFA)₂(*rcct*-tpcb)] was proposed from analytical and spectroscopic data. When the powder was recrystallized from MeOH, two types of crystals were isolated. Of these, the one that came out has 1D CP with 1,2-pyridyl groups involved in the connectivity instead of the expected 1,3-pyridyl groups of the *rtct*-tpcb due to structural rearrangement during crystallization. The second type of crystals obtained after a few days has the

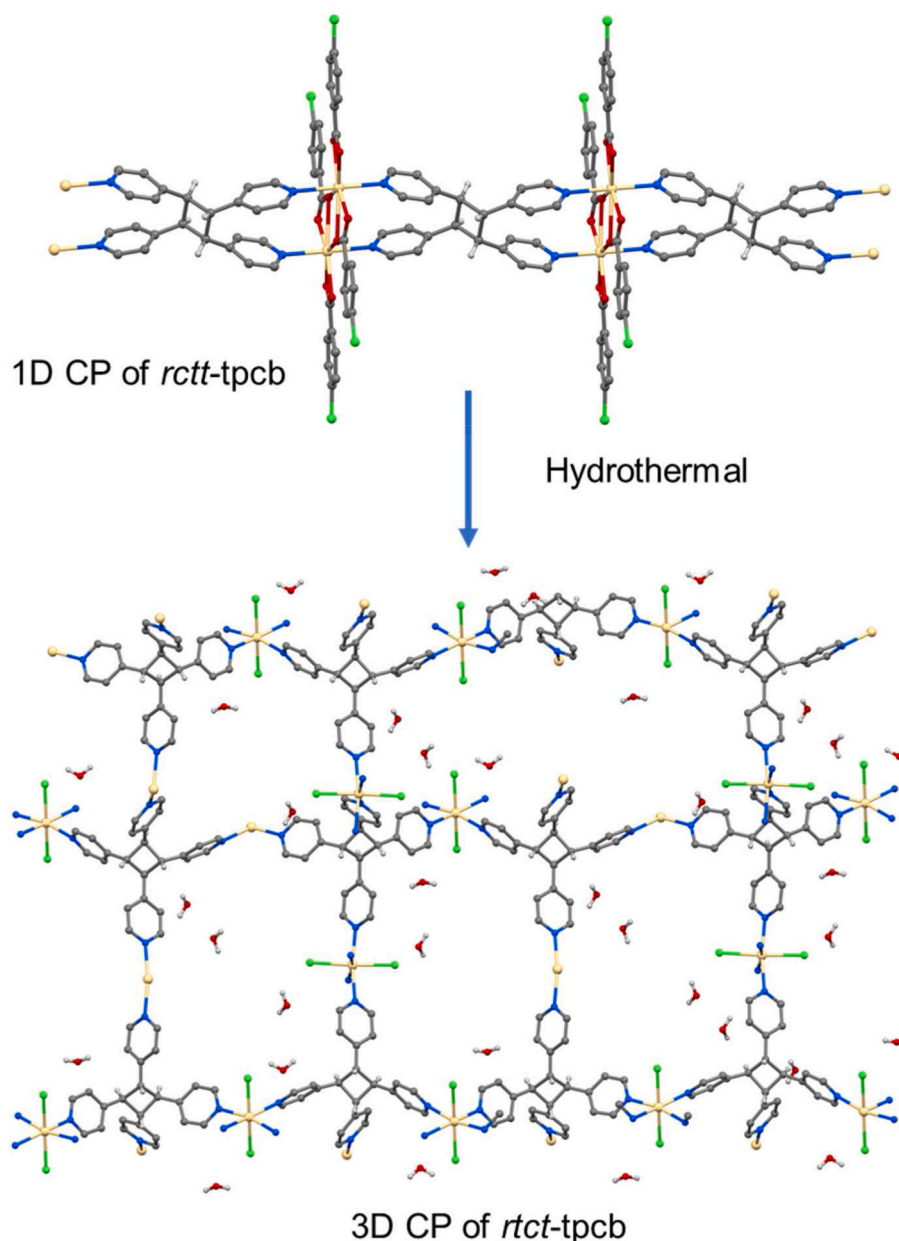


Fig. 5. Isomerization of *rctt*-tpcb to *rtct*-tpcb within coordination polymers under hydrothermal condition in the presence of acid.

same molecular formula but contains the *rttt*-isomer of tpcb (Fig. 9a). The connectivity in Fig. 9b shows that it is a 2D MOF [42].

The $^1\text{H-NMR}$ spectra of $[\text{Pb}(\text{TFA})_2(\text{rctt-tpcb})]$ in $\text{DMSO-}d_6$ after two days shows the presence of *rtct* and *rttt*-isomers in addition to *rctt*-isomer which was exclusively present at the beginning. Detailed investigations showed that the protonation of pyridyl group is responsible for the isomerization of *rctt*-isomers to other two isomers [43,44]. Although three isomers were present in solution, only two isomers were incorporated into MOFs, which could be attributed to the experimental conditions employed.

It is important to note that while *rctt*-tpcb act as square planar tetratopic building unit, *rtct*-tpcb on the other hand acts as a tetrahedral building unit. Isolated *rtct*-tpcb was incorporated into two metal organic frameworks, namely, $[\text{Zn}(\text{rtct-tpcb})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 6.5\text{H}_2\text{O}$, and $[\text{Co}(\text{rtct-tpcb})\text{F}_2] \cdot 5\text{H}_2\text{O}$. While the structure of the former consists of three-dimensional nets with **ptt** (twisted **pts**) topology, the latter was found to be a doubly interpenetrated 3D network with **pts** topology (Fig. 10). Thus, these two MOFs can be considered as topological isomers,

obtained by using two stereoisomers of a cyclobutane compound [22].

Two photoreactive supramolecular isomers of $[\text{Mn}(\text{NCS})_2(\text{OH}_2)_4] \cdot 4(2,2'\text{-bpe})$, which differ in the packing of the guest (2,2'-bpe). In one isomer, these alkene groups are arranged in a crisscross manner and in the second isomer, they are arranged in parallel. The crisscross alignment of the alkene pairs lead to the formation of *rtctt*-isomer, whereas the parallel disposition of the alkene pairs yielded the expected *rctt*-isomer as confirmed from the $^1\text{H-NMR}$ spectroscopic data [45]. On the other hand, cocrystals of 2,2'-bpe with mesaconic acid under UV irradiation produced *rctt*-, *rttt*- and *rtct*-isomers in the ratio of 76, 21 and 3% respectively. Interestingly, concomitant [2 + 2] cycloaddition addition occurred in the cocrystals of 2,2'-bpe and fumaric acid forming cyclobutane derivatives from both base and acid [46].

An interesting 1D CP, $[\text{Mn}(\text{NCS})_2(\text{rttt-2,4'-tpcb})]$ was obtained when UV-irradiated $[\text{Mn}(\text{NCS})_2(2,4'\text{-bpe})_2(\text{H}_2\text{O})_2]$ solid was refluxed in a water-methanol mixture. This is due to isomerization of the *rctt*-isomer under reflux conditions. The two 4-pyridyl groups were involved in bonding to Mn(II) in this CP as displayed in Fig. 11 [47].

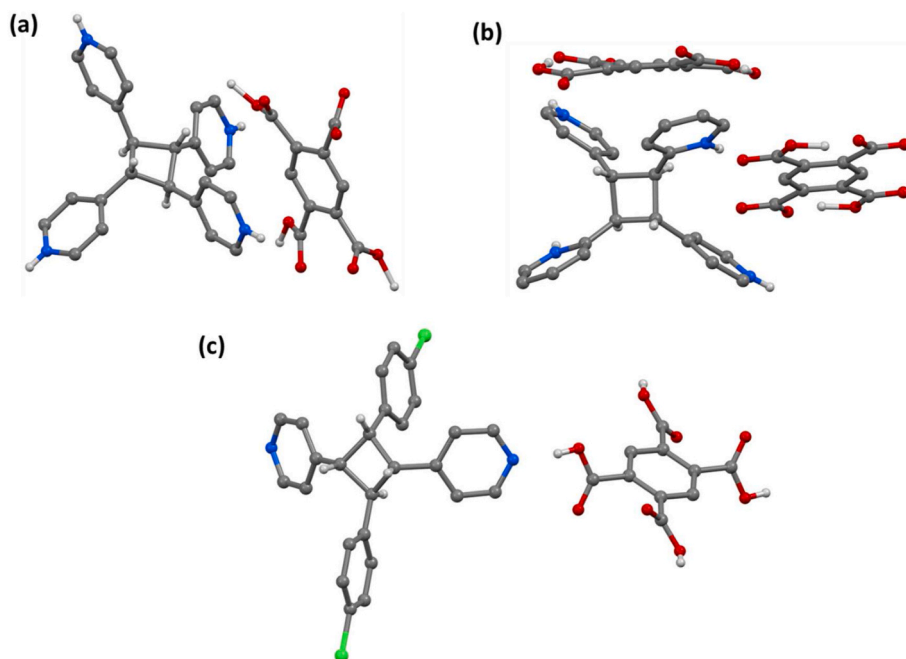


Fig. 6. Crystal structures of the dimers obtained after hydrothermal treatment. (a) $[(bta^{2-}) \cdot (rtct-4,4'-H_2tpcb)^{2+}]$ salt, (b) $[(bta^{2-}) \cdot \frac{1}{2}(rtct-2,4'-H_4tpcb)^{2+}]$ salt, and (c) $(rcct-4-Cl-dpcb) \cdot (bta)$ cocrystal. Lattice water molecules are not shown.

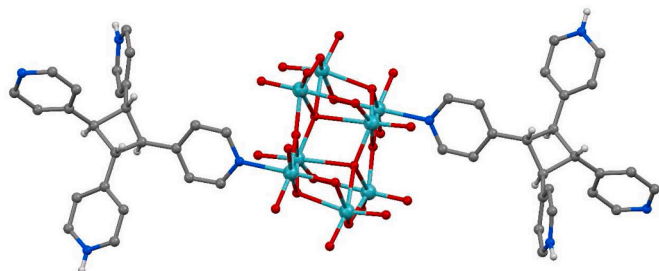


Fig. 7. Inorganic-organic hybrid solids obtained with *rtct*-tpcb and poly-molybdate. Two pyridyl groups are found to be protonated.

6. Formation of unusual isomers of cbtc rings by solvo/hydrothermal synthesis

During the photoreactions of a 2D MOF $[Cd_2(fumarate)_2(H_2O)_4]$, the presence of crisscross alignment of the fumarate ligands between the adjacent CP layers separated by 3.38 Å made the researchers to propose the formation of the *rtct*-isomer. The quantitative formation of *rtct*-cyclobutane-1,2,3,4-tetracarboxylate was monitored by the appearance of the *singlet* at 3.31 ppm due to the cyclobutane C-H proton in the 1H -NMR spectrum of the dissolved product [48].

Isomerization of *rtct*-1,2,3,4-cyclobutanetetracarboxylic acid (H_4cbtc) under hydrothermal condition to the corresponding *rtct*-isomer was reported during the preparation of a MOF [43]. In this, Kim et al. reported that *rtct*- H_4cbtc when exposed to hydrothermal heating under alkaline condition in the presence of KOH and Lanthanum(III) chloride, it yielded a coordination polymer with open framework of composition $[La(OH_2)(Hcbtc^{3-})]$, where the ligand was found to have undergone isomerization to *rtct*-form (Fig. 12) [49]. Isomerization of *rtct*-1,2,3,

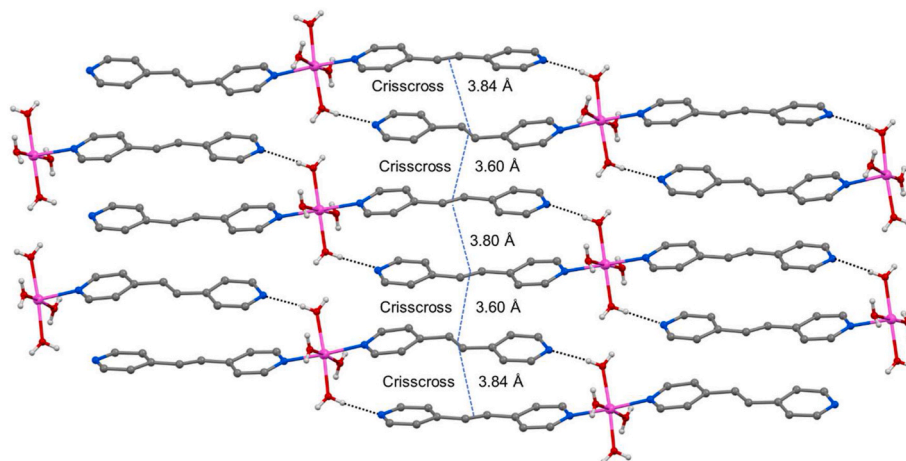


Fig. 8. Packing of the $[Zn(bpe)_2(H_2O)_4]^{2+}$ complex showing the supramolecular interactions in the cationic layer, crisscrossed arrangements of bpe within distances suitable for photodimerization. Anions, lattice water molecules, and hydrogen atoms are omitted for clarity.

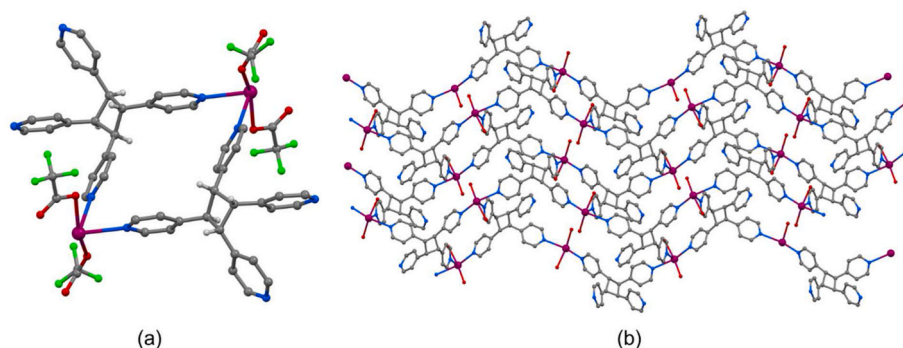


Fig. 9. (a) A part of the MOF showing the connectivity around the Pb(II) atoms and *rcct*-tpcb; (b) Connectivity showing the corrugated sheet structure. Only relevant atoms are shown for clarity.

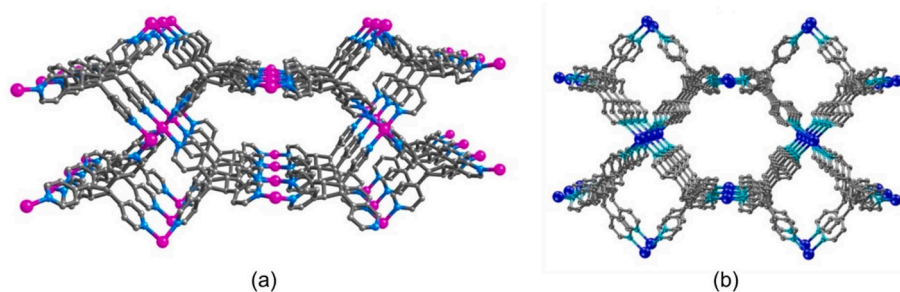


Fig. 10. a) *ptt* topology. b) *pts* topology Copyright © 2010 American Chemical Society (Ref. 22).

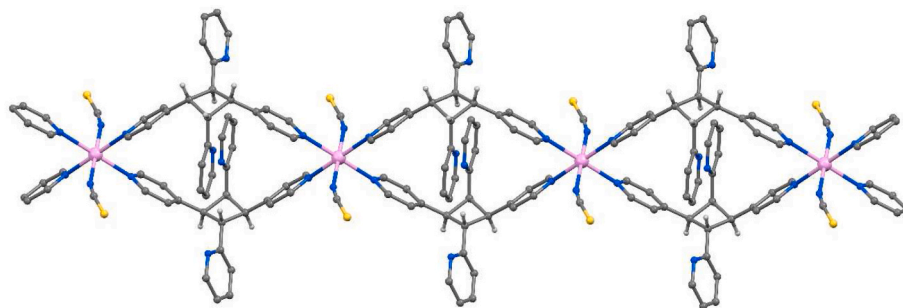


Fig. 11. Connectivity of the isomer *rtct*-2,4'-tpcb in the 1D CP.

4-cyclobutanetetracarboxylic acid (*rcct*-H₄cbtc) to *rtct*-H₄cbtc was also observed by Briceño et al. when the powdered (Im⁺)₂[(*rcct*-H₂cbtc)²⁻] (Im = imidazole) was heated under hydrothermal conditions at 140–190 °C for 2 days. This was confirmed by ¹H NMR spectroscopy [50].

7. Chemical transformation of cyclobutane compounds

Another type of isomerization associated with chemical transformation was observed in the solid state for *trans,trans*-muconate (*tr, tr*-muco) ligand that has two conjugated ethene substituents at 1,2 positions, and when they have parallel orientation satisfying the Schmidt's criteria for photoreaction. Such dispositions can offer multiple options that lead to the formation of different photoproducts. For instance, it can either lead to the formation of ladderane by stitching all the C=C bonds via double [2 + 2] cycloaddition reaction, or it can lead to the formation of a cyclooctadiene ring via a [4 + 4] cycloaddition reaction. In both these cases, both the pair of C=C bonds are involved in the photoreaction. The third possibility is that only one pair of C=C bonds is involved first to produce a cyclobutane ring and the other unreacted C=C bond

pairs, if aligned in parallel, may involve in further reaction like 1,3-sigmatropic rearrangement or Cope rearrangement (Fig. 13) [51]. It can be noted that only the *rcct*-form of the cyclobutane compound can undergo Cope rearrangement, not the *rtct*-form.

The sodium and potassium salts of *tr, tr*-muconic acid exhibited interesting features of photodimerization reaction. Crystal structure determination of these salts show the infinite parallel stacking of the C=C bonds and resulted in the formation of the *rcct*-form of a cyclobutane product via dimerization between a single pair of C=C bonds, followed by Cope rearrangement to yield cycloocta-3,7-diene-1,2,5,6-tetracarboxylate. Here, the cyclobutane compound (dimer A in Fig. 13) act as the intermediate of this consecutive reaction. The course of the reaction, i.e., formation of the intermediate cyclobutane compound and the cyclooctadiene as the final product was monitored by NMR spectroscopy. A 'percent conversion versus time' plot (Fig. 14) shows the intermediate goes towards zero through a maxima, the typical characteristics of a consecutive reaction [52].

It is important to note here that the formation of ladderane as the sole product was observed with ester [53] and pyridyl [54] systems, and in a gold(I)-macrocycle, the *tr, tr*-muconate ligand was found to undergo [4

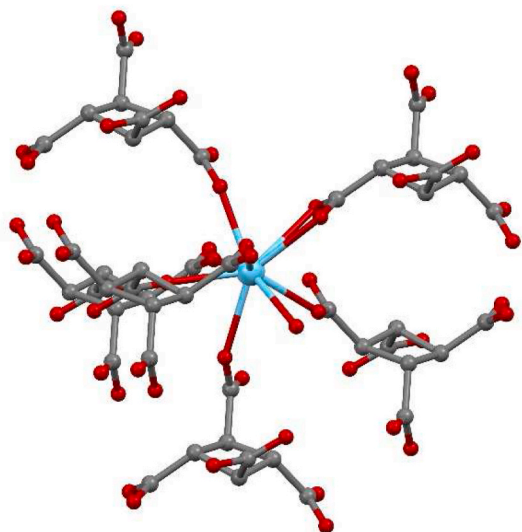


Fig. 12. Coordination environment of La in coordinatuon polymer, showing the isomerization of *rcctt*-cbtc to *rtctt*-cbtc.

+ 4] cycloaddition reaction in a single step to yield cycloocta-3,7-diene-1,2,5,6-tetracarboxylate as the sole product quantitatively [55], which are significantly different cases of photoreaction than that was observed with these salts. It is still not clearly understood when a system, having parallel stacking of two consecutive C=C bonds, would undergo a double [2 + 2] cycloaddition reaction to yield a ladderane, undergo a single step [4 + 4] cycloaddition reaction, or a stepwise [2 + 2] cycloaddition reaction followed by Cope rearrangement to yield a cyclooctadiene compounds. More synthetic and theoretical works are necessary to understand deeply about the chemical reaction dynamics of such systems.

8. Conclusion

Herein, we reviewed the literature on the isomerization of pyridyl-substituted cyclobutane ligands, its salts, in CPs and MOFs, in the solid state as well as in solution. The commonly observed *rcctt*-isomer is

the geometry driven kinetic product, which can isomerize to the thermodynamically most stable *rtctt*-form by heating in both the solution and solid-state. Isomerization can even lead to the formation of rare *rcctt*-isomers which are intermediate forms and are neither kinetically nor thermodynamically favoured structures. It is interesting to note that there is no ring cleavage observed during this process despite strain in the four membered ring.

While solution-phase isomerization is very common, isomerization in the solid state is rather rare. In addition, cyclobutane compounds often undergo thermal-cleavage, leading to the formation of the monomers back. Therefore, isomerization and thermal cleavage can be two competing processes in the solid state. Other than cyclobutane ring compounds, cyclooctadiene is also another ring compounds whose isomerization, or its formation via Cope rearrangement has well been investigated in the solid state. No doubt, such processes offer opportunities to access rare isomers of the ring compounds. Isomerization is, therefore, a viable route to access rare isomers of functional cyclobutane

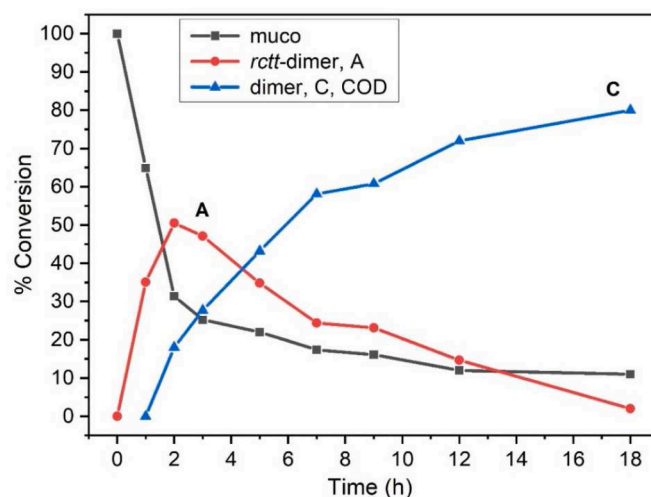


Fig. 14. Plot of 'percent (%) conversions versus time' for (a) Na_2muco , which shows the cyclobutane dimer (A) is the intermediate of a consecutive reaction that finally yields cyclooctadiene (C) dimer.

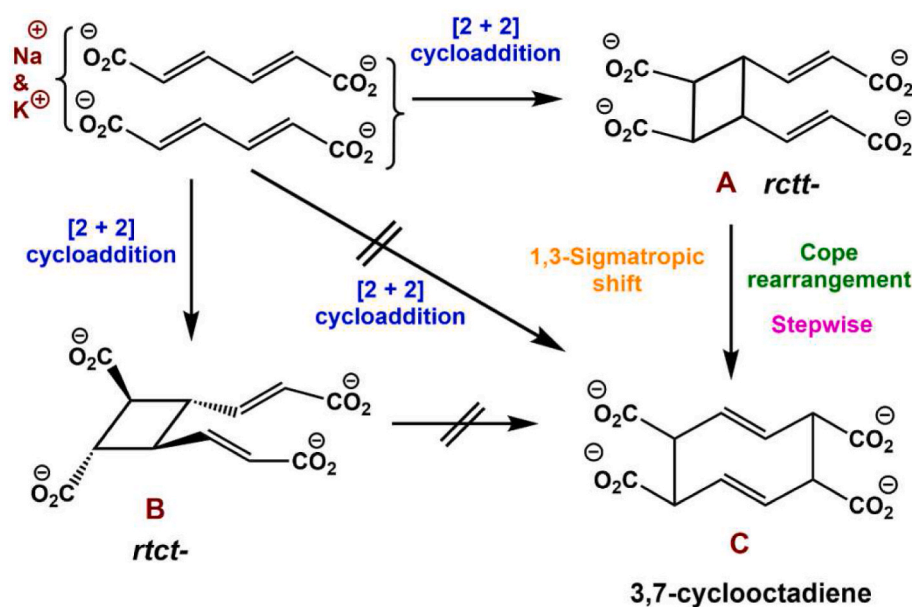


Fig. 13. Schematic representation of observed photoreactivity of Na-, and K-salts of *tr, tr*-muco. First a cyclobutane dimer (A) is formed, which transforms to cyclooctadiene (C) via Cope rearrangement.

compounds, which in turn have been employed to construct topological architectures. Thus, it plays an important role in synthetic chemistry.

Ethics approval and consent

This study has nothing to do with human and animal testing.

Consent for publication

All the authors giving their consent to publish the current manuscript.

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Contribution by principal cum corresponding author

JJV proposed and initiated this review. The critical revision of the manuscript and final approval of the version were done by both the authors.

Contribution by other author

The first author is also a corresponding author and shared the responsibility with the second author.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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