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LETTER

Combining topochemical [2 + 2] photoreactions and hydrothermal isomerisation for the regioselective and quantitative preparation of *rtct*-pyridylcyclobutanes†

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A non-photochemical route for the regioselective and quantitative preparation of *rtct*-pyridylcyclobutane isomers is achieved from the combination of solid state [2 + 2] photoreactions and controlled isomerisations promoted either by Lewis or Brønsted acids under hydrothermal conditions.

Recent efforts have been made in the implementation of supramolecular strategies to direct reactivity of olefins either in the solid state[1–3] or in solution.[4] In both cases, supramolecular assistance based on the use of auxiliary molecules, and/or metal centres is commonly used to drive regiocontrolled synthesis of single cyclobutane stereoisomers. Particularly, in the solid state such strategies provide an exquisite regio- and stereoselective control combined with quantitative yields.[1–3] However, in spite of the well known advantages of solid state reactions over the same reactions in solution, such strategies have been successful almost exclusively in obtaining *rctt*-cyclobutane-like compounds, but are unsuitable for preparation of other stereochemical configurations that are difficult to access (*i.e.*, *rcct*, *rtct* and/or head-to-tail isomers). The preference for this configuration is a direct consequence of the *syn* orientation of the available functional groups commonly used on the homo-template (–OH, COOH and pyridines) exploited for the alignment of the olefins.[1c] Interestingly, although this stereochemistry is not the most thermodynamically stable, it is the most favourable in the products obtained from direct irradiation of olefins also in solution.[5] Thus, the development of strategies focused on the improvement of regioselective synthesis of not easily accessible cyclobutanes continues to be an exciting challenge in organic photochemistry. In this regard, we reported the combination of topochemical cycloaddition with hydrothermal methods for the regioselective preparation of different *rtct*-pyridylcyclobutanes promoted by polymolybdates (POMs).[6a] These isomers were isolated as counterions into inorganic–organic hybrid solids and obtained in high to fair yields. Likewise, we reported the asymmetrical thermal stereomutation of head to tail *rctt*-1,3-bis(2-pyridyl)2,4-bis(4-pyridyl)cyclobutane [*rctt*-2,4-tpcb-ht; tpcb = tetrapyridylcyclobutane] to the *rttt*-isomer *via* metal assistance (Mn^{2+}).[6b] Later, Vittal and co-workers have reported that the photoproduct from 4,4′-bpe (*rctt*-4,4-tpcb) isomerizes slowly in solution to the *rcct*- and *rtct*-isomers at room temperature catalyzed by CF_3CO_2H acid.[7a] Also, the same dimer at 100 °C undergoes a quantitative conversion to the *rtct*-4,4-tpcb isomer in the presence of either trifluoroacetic acid or HCl.[7b,8] Based on these antecedents, we have evaluated different factors such as: electronic effect of the relative position of the N atom on the pyridyl ring, temperature, heating time, metal centres and acid assistance, among others in order to tune quantitative transformations. Herein the potential of such a strategy is demonstrated by the synthesis, structural characterisation, solid state reactivity and isomerisation studies of different *rctt*-stilbene dimers (Scheme 1). The ^1H-NMR characterisation of the organic products obtained under different experimental conditions reveals the selective isomerisation of the different *rctt*-dimers into *rcct*-, or *rtct*-isomers, depending on temperature, metal or acid assistance. Under hydrothermal conditions, quantitative isomerisation of *rctt*-dimers into *rtct*-dimers was observed in all the cases.

The cyclobutane derivatives were prepared from controlled [2 + 2] cycloaddition reactions in the solid state of *trans*-bis(4-pyridyl)ethylene (4,4′-bpe), *trans*-bis(2-pyridyl)ethylene (2,2′-bpe) and *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4′-bpe), according to previously published procedures.[6,9,10] The different photo products obtained were characterised by ^1H-NMR spectroscopy before the isomerisation in order to verify the chemical purity of starting cyclobutanes (see ESI†).

Based on our earlier works,[6] we promptly evaluated the effect of the metal centre on the isomerisation of the photodimers, which were heated in the presence of Mn^{2+} and Al^{3+} metal centres upon reflux in methanol/water for 24 h. The ^1H-NMR characterisation of the products isolated after the thermal treatment confirmed the isomerisation of some cyclobutane derivatives. The spectra showed the presence of the same signals observed for starting compounds, together with

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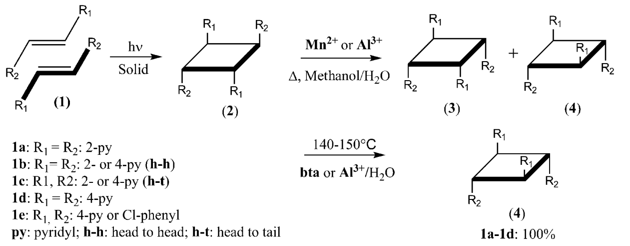

Scheme 1

an additional complex set of signals characteristic of an asymmetrical product. These changes can be easily monitored in the region of the aliphatic methine protons (3–5.4 ppm, see ESI†). All the compounds undergo partial isomerisation to give *rcct* and *rctt* mixture in different ratios, depending on the starting compound, except for the dimers from 2,2′-bpe and 2,4′-bpe (h–t), where the partial formation of the *rtct*-isomers was also observed in the ^{1}H-NMR spectra. The compositions of the resulting mixtures were determined by ^{1}H-NMR analysis and are summarised in Table 1. In all the cases the isomerisation degree was always slightly higher in the presence of Al^{3+} than Mn^{2+} solution. It is important to note that the formation of *rcct* isomers is not commonly observed, to our knowledge, from direct photoreaction of stilbenes in solution,[4f,7b,8] the *rctt*-isomer always being the favoured one. Nevertheless, under such conditions it is possible to achieve moderate yields (36–52%), such a possibility can be viewed as a useful route to drive the synthesis of these stereoisomers. In addition, the *rcct*-isomer obtained from the isomerisation of **1b** yields a chiral isomer (Fig. S6, ESI†). This result suggests that this route can also be exploited in order to induce chirality from achiral cyclobutane derivatives.[12]

Encouraged by these results, we evaluated the effect of Al^{3+} salt on the same transformations under hydrothermal conditions at 140 °C for 24–48 h, in order to achieve quantitative conversions. On the other hand, the Mn^{2+} ion was discarded in the study under hydrothermal conditions due to the effect of a paramagnetic ion on NMR line broadening, which is difficult to be removed completely from the solution. The ^{1}H-NMR spectrum of the products obtained after the hydrothermal treatment either of the mixture obtained from the study upon reflux in the presence of Al^{3+} or using fresh *rctt*-dimers did not show the presence or formation of asymmetrical stereoisomers (*rcct*), in contrast to those cases described above. The signals observed display different chemical shift values compared to the corresponding protons in the starting *rctt*-isomers. These values are characteristic of different symmetrical isomers (*rtct*-configuration).[5] All the spectra revealed a quantitative isomerisation (100%). In order to gain better insight about this process, a new set of experiments in the presence of a Brønsted-acid were also evaluated. Thus, taking advantage of the use of 1,2,3,4 benzenetetracarboxylic acid (bta) as an efficient template to direct reactivity of olefins in the solid state and its ability to give interesting supramolecular assembly directed by charge-assisted hydrogen bonds,[11] here, we extended the use of bta either to assist the isomerisation process or as a potential crystallisation agent of the resulting isomers. The dimers were heated at 140 °C in the presence of bta under hydrothermal conditions, using bta : dimer in a molar ratio 1 : 1. The ^{1}H-NMR spectra showed similar results to those observed for the isomerisation in the presence of Al^{3+} (quantitative isomerisation into the *rtct*-isomer). As anticipated, the resulting stereochemistry for *rtct*-4,4′-tpcb and *rtct*-2,4′-tpcb-ht isomers was confirmed by single crystal X-ray diffraction analysis. Crystals of $[(bta^{2-})\cdot(rtct\text{-}4,4'\text{-}H_2tpcb)^{2+}]\cdot 5H_2O$ (**5**) and $[(bta^{2-})\cdot(rtct\text{-}2,4'\text{-}H_4tpcb\text{-}ht)_{0.5}{}^{4+}]\cdot 1.28H_2O$ (**6**) were obtained by crystallisation of corresponding bta–*rtct*-isomer mixture after heating.

The asymmetric unit of **5** contains half stilbenium (*rtct*-4,4′-tpcb)$^{2+}$ cation lies on a twofold-axis, one bta^{2-} anion and five disordered lattice water molecules.‡ The crystal structure of **5** forms a 3D-hydrogen bonded network (Fig. 1(a)), which can be described as 2D-hydrogen bonded layers built-up from self-assembly of bta^{2-} anions linked by charge-assisted hydrogen bonding between carboxylic and carboxylate groups [O1· · ·O5: 2.492(4) and O7· · ·O3: 2.526(4) Å] (Fig. 1(b)). Such H-bonded networks are extended in the *bc*-plane and display rhomboidal windows with distances *ca.* 7.2 × 8.7 Å. In each layer, every window is penetrated by one 4-pyridyl unit from $(rtct\text{-}4,4\text{-}H_2tpcb)^{2+}$ cations, whereas the remaining pyridyl moieties are oriented parallel to 2D-hydrogen networks. These cations are distributed above and below these layers in an alternate fashion. These layers are sustained through multiple hydrogen bonding interactions among pyridinium, pyridyl, carboxylate and carboxylic moieties and disordered lattice water molecules located into intricate channels that run along

Table 1 Product distribution of **1a–1e** isomers determined by ^{1}H-NMR at different thermal conditions; upon reflux or hydrothermal conditions (HC) in the presence of Mn^{2+}, Al^{3+} or bta

	Reflux with Mn^{2+}			Upon HC with Al^{3+} or bta		
Dimer	**2**	**3**	**4**	**2**	**3**	**4**
1a	44	—	56	—	—	100
1b	62	38	–	—	—	100
1c	52	48	–	—	—	100
1d	54	46	–	—	—	100
1e	—	—	—	14	86	—
	Reflux with Al^{3+}					
1a	44	—	56			
1b	59	41	—			
1c	13	49	38			
1d	48	52	—			

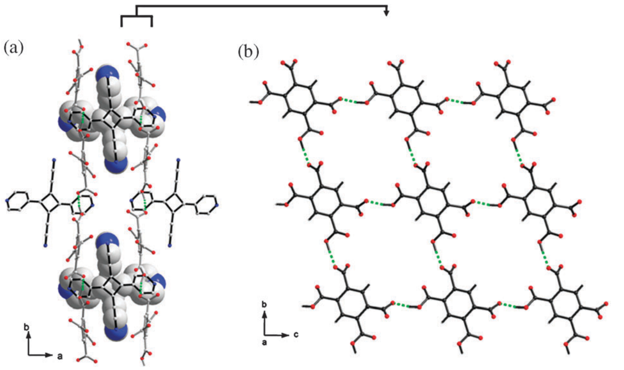

Fig. 1 (a) View of the stacking of the crystal structure of **5**. (b) 2D H-bonded network formed by charge-assisted hydrogen bonding between anions in the *bc*-plane.

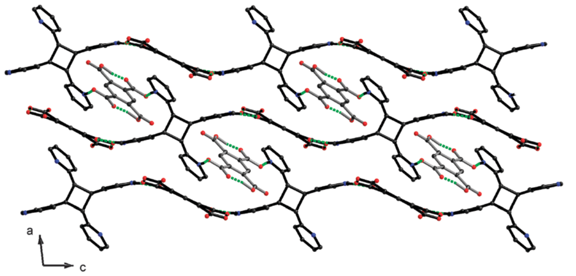

Fig. 2 View of the H-bonded layers linked by the charge-assisted carboxylate–pyridinium hydrogen bonds in the structure of **6**.

the *b*-direction. The percentage of solvent-accessible space in these channels in the crystal structure corresponds to 21.8% (2132 $Å^3$ per unit cell) of the total volume (9780 $Å^3$).

The asymmetric unit of **6** contains one half stilbenium (*rtct*-2,4′-tpcb)$^{4+}$ cation lies about a twofold axis, two halves of crystallographically independent bta^{2-}anions, one is located on a twofold axis, while the other lies about an inversion centre and one water of crystallisation with partial occupation. The crystal structure of **6** forms a 3D-hydrogen bonded network (Fig. 2), which can be seen as a sinusoidal 2D-hydrogen bonded network self-assembled from bta^{2-} anions linked by charge-assisted carboxylate–pyridinium supramolecular synthons. This array is constructed from zigzag ribbons connected *via* charge assisted hydrogen bonding between one bta^{2-} anion and 4-pyridinium units from the (*rtct*-2,4′-H$_4$tpcb-ht)$^{4+}$ unit along the *c*-direction [N1···O1: 2.657(3) Å]. These ribbons are linked by the second bta^{2-} anion through remaining 2-pyridyl units from (*rtct*-2,4′-H$_4$tpcb-ht)$^{4+}$ cations also *via* carboxylate–pyridinium interactions [N2···O8: 2.405(3) Å]. These interactions generate H-bonded layers parallel to the *ac*-plane. Adjacent layers are stacked *via* self-complementary hydrogen bonding between water molecules of crystallisation and oxygen atoms of carboxylic groups. In this structure the preferred formation of intramolecular hydrogen bonds between carboxylate and carboxylic groups is observed, in contrast to that observed for **5**.

Encouraged by the above results, we have expanded the tolerance of this approach in relation to stilbazole derivatives. In particular, the isomerisation from the *rctt*-head to tail dimer of 4-Cl-Stb (*rctt*-4-Cl-dpcb-ht) under hydrothermal conditions at 140 °C leads to the formation exclusively of the asymmetrical stereoisomer (*rcct*) in high yield *ca.* 86%, in contrast to those cases found using stilbene derivatives. A remarkable feature in these processes is the apparent isomerisation of the pyridyl ring. Suitable crystals bearing bta-*rcct*-4-Cl-dpcb-ht isomer mixture (**7**) were also obtained. The asymmetric unit of **7** contains one molecule of the resulting dimer located in a general position with no imposed symmetry; one half of bta lies about an inversion centre, and one water of crystallisation with partial occupation. The crystal structure of **7** forms 1D-hydrogen bonded chains self-assembled *via* heterodimeric hydrogen-bonded synthons based on the interaction between carboxylic and pyridyl groups in an alternate fashion, producing hydrogen bonded rings along the (101)-direction [N1···O3: 2.594(3) and N2···O2: 2.725(3) Å] (Fig. 3). Such interactions are neutral in contrast to those observed for **5** and **6**.

A striking feature of the isomerisation processes observed for the different tpcb is that these did not occur when the reactions were carried out in the absence of metal centres or bta under identical experimental conditions. In addition, in these assays the formation of side products due to the cycloreversion reaction and/or other asymmetrical stereomutations was not observed, in contrast to the thermal isomerisation of cyclobutanes at elevated temperatures.[12] These results reveal the regio- and stereospecific nature of all the isomerisations upon hydrothermal control.

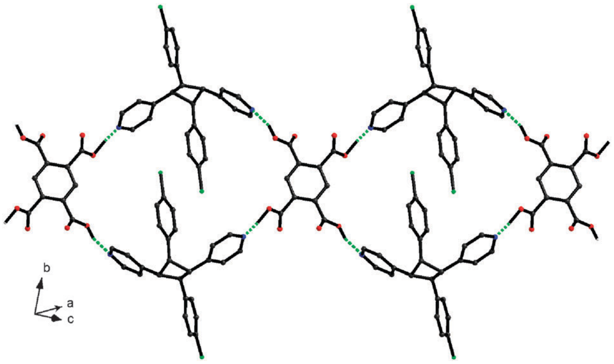

Fig. 3 View of H-bonded chains in the crystal structure of **7**.

At the present stage, based on these observations and further examination of our previously reported works on isomerisation of pyridyl cyclobutanes some insight can be drawn: (a) the isomerisation of this kind of compounds is closely related to the intrinsic strain associated with a four membered ring combined with repulsive electrostatic charges generated for the presence of ionisable groups (pyridyl and –COOH) on the rings.[6,13] In particular, a remarkable electronic effect either of the relative position of the N atom on the pyridyl ring or the presence of neutral substituent groups is observed. (b) Either acidity or temperature plays a fundamental role in the stereoselective control of the resulting isomers, where the *rcct*-isomer is a metastable intermediate, which is formed in a first step upon mild heating, then is transformed to the most stable isomer (*rtct*) at highest temperatures. Similar results have been observed by Vittal *et al.*,[7] in the isomerisation of *rctt*-4,4′-tpcb to *rtct*-isomer promoted by HCl. (c) The intelligent choice of the substituent groups on the cyclobutane ring can be exploited to fine-tune quantitative and regio- and stereoselective synthesis either of *rcct* or *rtct* isomers, depending on temperature.

In summary, we have demonstrated the ability either of a Lewis or Brønsted acid combined with an increase in temperature to promote the partial or total isomerisation in solution of *rctt*-isomers either to *rcct* or *rtct*. We have established a non-photochemical route to prepare quantitatively and regio- and stereoselectively *rtct*-tpcb compounds *via* hydrothermal-assisted isomerisation. This novel approach opens a window to develop efficient routes for the preparation and/or improvement of the yield of new and conventional cyclobutane-like stereoisomers that are difficult or impossible to access either in solution or by known solid state routes, including the possibility of obtaining chiral cyclobutanes. This alternative can be very helpful in order to overcome the limitations imposed by the topochemical postulate[14] for obtaining regioselective photoproducts with such stereochemical requirements from crystalline assemblies. In addition, these *rtct*-cyclobutane derivatives represent novel attractive multitopic building blocks for the self-assembly of metal–organic polyhedra,[15] MOFs,[1b] supramolecular hydrogen bonded assemblies and particularly the study of supramolecular isomerism.[9a,16] Further works on the use of such molecules in the self-assembly of multicomponent supramolecular arrays, as well as the induction of chirality on achiral cyclobutane derivatives *via* hydrothermal isomerisation are in progress.

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Notes and references

‡ Crystal data for **5**: $C_{22}H_{26}N_2O_{13}$, M_t = 526.45, orthorhombic, space group *Fdd*2, T = 293(2) K, a = 27.455(7), b = 36.891(9), c = 9.656(2) Å, U = 9781(4) Å^3, Z = 16, μ(Mo-Kα) = 0.12 mm^{-1}, ρ_{calcd} = 1.430 g cm^{-3}. R_{int} = 0.035, $R_1(F^2)$ = 0.058, $wR(F^2)$ = 0.16, S = 1.050 for 3579 independent reflections ($I > 2\sigma(I)$). CCDC 831805. Crystal data for **6**: $C_{44}H_{34.56}N_4O_{17.28}$, M_t = 895.80, monoclinic, space group $P2/n$, T = 293(2) K, a = 11.2070(18), b = 10.5278(15), c = 17.198(3) Å, β = 96.718(4), U = 2015.1(5) Å^3, Z = 2, μ(Mo-Kα) = 0.12 mm^{-1}, ρ_{calcd} = 1.476 g cm^{-3}. R_{int} = 0.037, $R_1(F^2)$ = 0.058, $wR(F^2)$ = 0.16, S = 1.04 for 2878 independent reflections ($I > 2\sigma(I)$). CCDC 831806. Crystal data for **7**: $C_{62}H_{47.24}Cl_4N_4O_{8.63}$, M_t = 1128, triclinic, space group $P\bar{1}$, T = 293(2) K, a = 10.254(3), b = 10.381(3), c = 13.085(5) Å, α = 86.63(3), β = 87.56(3), γ = 75.39(2)°, U = 1344.9(7) Å^3, Z = 2, μ(Mo-Kα) = 0.284 mm^{-1}, ρ_{calcd} = 1.393 g cm^{-3}. R_{int} = 0.024, $R_1(F^2)$ = 0.052, $wR(F^2)$ = 0.153, S = 1.05 for 4015 independent reflections ($I > 2\sigma(I)$). CCDC 831807.

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