

# A Regiocontrolled ‘Head-to-Tail’ [2 + 2] Photodimerization of a Stilbene Involving a Ternary Solid Based on Catechol

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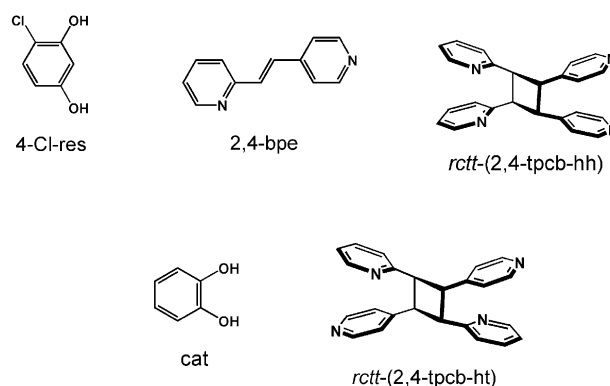
**Abstract**—Co-crystallization of 1,2-dihydroxybenzene (cat) with *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4-bpe) gives a layered ternary solid, (cat)·(2,4-bpe)·(H<sub>2</sub>O) **1**, with molecular components held together by a combination of O–H···N and O–H···O forces wherein 2,4-bpe is organized for a ‘head-to-tail’ (ht) [2 + 2] photocycloaddition. UV-irradiation of the solid produces *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane [*rctt*-(2,4-tpcb-ht)] in quantitative yield. The structure of *rctt*-(2,4-tpcb-ht), in the form of crystalline *rctt*-(2,4-tpcb-ht)·1.5(H<sub>2</sub>O), has been confirmed by way of single-crystal X-ray diffraction.

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We have recently introduced a method for directing the photoinduced [2 + 2] cycloaddition reaction in the solid state using molecules that function as linear templates.<sup>1,2</sup> The approach eliminates many vexatious problems of weak intermolecular forces that have made the reaction difficult to control. It is now possible to direct the photoreaction regioselectively and utilize the reaction to conduct molecular solid-state synthesis by design. Co-crystallization of 4-chlororesorcinol (4-Cl-res) with *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4-bpe), for example, has been shown to give a four-component molecular assembly, 2(4-Cl-res)·2(2,4-bpe), held together by four O–H···N hydrogen bonds, wherein two bipyridines are preorganized by the diol for a ‘head-to-head’ (hh) photocycloaddition.<sup>3</sup> Ultraviolet (UV) irradiation of the solid produced the desired product, *rctt*-1,2-bis(2-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (*rctt*-2,4-tpcb-hh), regioselectively in quantitative yield (Scheme 1). We have also demonstrated that products derived from this solid-state approach may be utilized as ligands for the construction of transition-metal-based coordination arrays, the templates dictating the structures of the ligands and resulting metal-organic products.<sup>3,4</sup>

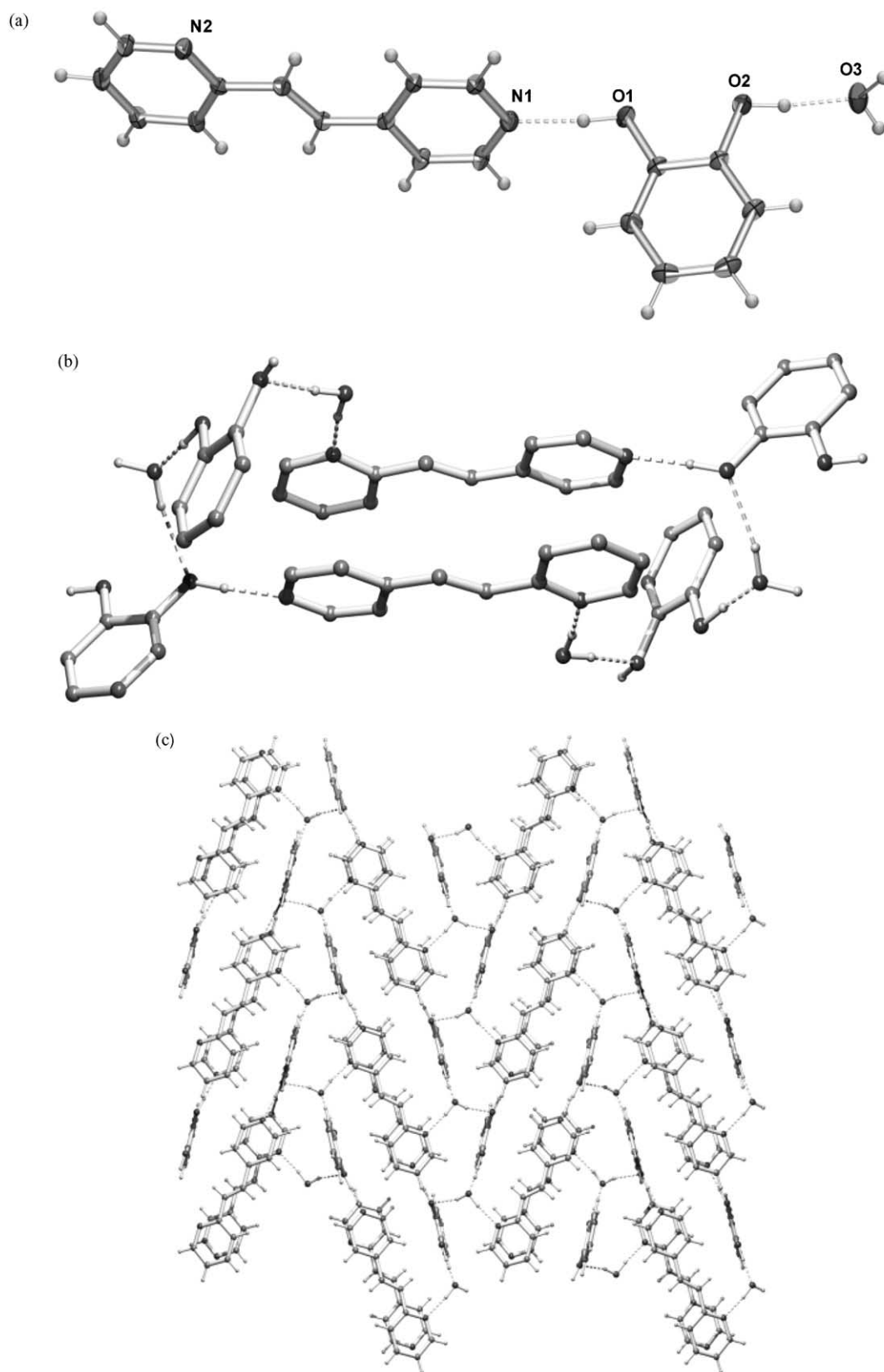
During studies aimed to expand this solid-state approach to additional templates, we have discovered

the ability of 1,2-dihydroxybenzene, or catechol (cat), to assemble with 2,4-bpe and adventitious water molecules to produce a layered ternary solid, (cat)·(2,4-bpe)·(H<sub>2</sub>O) **1**, wherein the stilbene is organized, by way of hydrogen bonds, in a position suitable for a ‘head-to-tail’ (ht) [2 + 2] photocycloaddition.<sup>5</sup> UV-irradiation of the multi-component solid produces *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (*rctt*-2,4-tpcb-ht), regioselectively (yield: 100%). In addition to providing access to the ‘head-to-tail’ regioisomer of *rctt*-2,4-tpcb, **1** provides insight into factors that lead to reactivity within multi-component crystalline solids, which is of much current interest.<sup>1,6</sup>



Scheme 1.

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**Figure 1.** Perspectives of the X-ray crystal structure of **1**: (a) hydrogen bonds involving the molecular components, (b) the double-layered herringbone structure, and stacking of the stilbenes (c) within and (d) between the herringbone framework. Selected interatomic distances (Å): O(1)···N(1) 2.694(3), O(2)···O(3) 2.644(1).

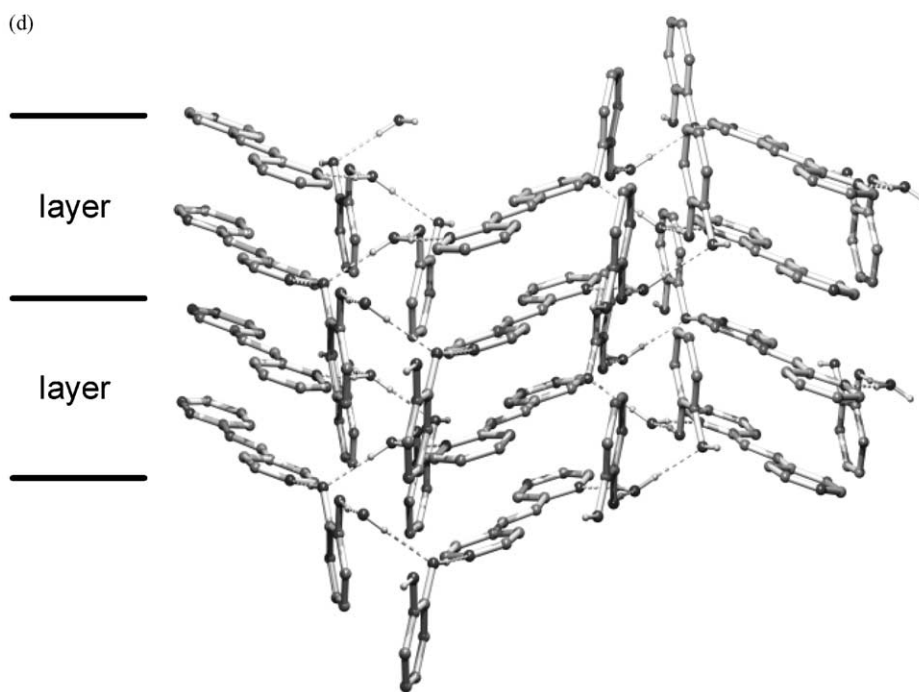


Figure 1. (continued)

Addition of cat (0.12 g) to acetone (10 mL) in the presence of 2,4-bpe (0.198 g) yielded, upon standing for a period of approximately 2 days, light yellow crystals of **1** (yield: 100%) suitable for X-ray analysis. The formulation of **1** was confirmed by  $^1\text{H}$  NMR spectroscopy and single-crystal, as well as powder, X-ray diffraction.<sup>7</sup>

A perspective view of the X-ray crystal structure of **1** is shown in Fig. 1. The components of **1** have assembled in the solid state by way of a combination of O–H $\cdots$ N and O–H $\cdots$ O forces. Specifically, a hydroxy group of cat,<sup>8</sup> similar to 2(4-Cl-res)-2(2,4-bpe), interacts with the 4-pyridyl group of 2,4-bpe by way of an O–H $\cdots$ N hydrogen bond [O(1) $\cdots$ N(1) 2.694(3) Å] such that the benzene unit is oriented approximately orthogonal with respect to the pyridyl ring [twist angle: 67.8(1) $^\circ$ ]. In this arrangement, the second hydroxyl group of cat participates in an O–H $\cdots$ O hydrogen bond with an included water molecule [O(2) $\cdots$ O(3) 2.644(1) Å]. The water molecule, in turn, serves as a bifunctional hydrogen bond donor, forming an O–H $\cdots$ N [O(3) $\cdots$ N(2)<sup>i</sup> 2.784(3) Å] and an O–H $\cdots$ O [O(3) $\cdots$ O(1)<sup>ii</sup> 2.840(1) Å] (symmetry operations: i:  $-x, 1-y, 2-z$ ; ii:  $x, 3/2-y, 1/2+z$ ) hydrogen bond with a 2-pyridyl unit and hydroxyl group of a second 2,4-bpe and cat molecule, respectively. As a consequence of these forces, the components of **1** form a double-layered herringbone<sup>9</sup> framework, within the crystallographic *bc*-plane (Fig. 1b), wherein the bipyridines stack ‘head-to-tail’ (Fig. 1c), interacting by way of  $\pi$ – $\pi$  interactions. Notably, the layers organize in the solid state such that bipyridines of adjacent layers are, similar to each layer, oriented in a ‘head-to-tail’ fashion, interacting by way of  $\pi$ – $\pi$  forces (Fig. 1d). The stacking of the olefins within and between the double layers of **1** results in the carbon-carbon double (C=C) bonds of 2,4-bpe, which lie disordered across two

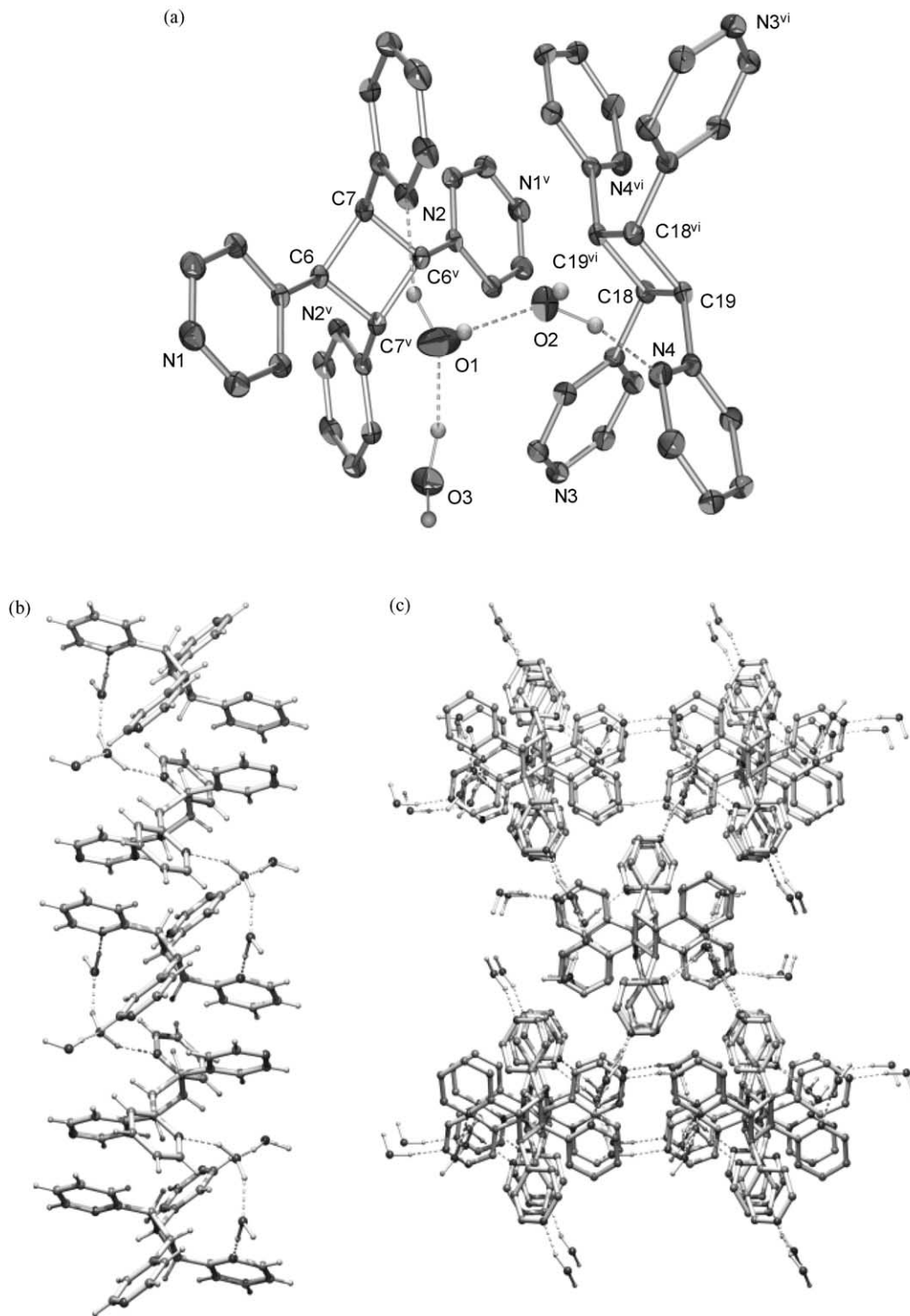
positions (occupancies: 85:15), being organized in a parallel fashion and separated by 3.80 Å (C $\cdots$ C separations (Å): 3.804(2) [C(6) $\cdots$ C(7)<sup>iii</sup> and C(7) $\cdots$ C(6)<sup>iii</sup>] [symmetry operations: iii:  $-x, -y+1, -z+1$ ] and 3.75 Å (C $\cdots$ C separations (Å): 3.749(2) [C(6) $\cdots$ C(7)<sup>iv</sup> and C(7) $\cdots$ C(6)<sup>iv</sup>] [symmetry operations: iv:  $-x+1, -y+1, -z+1$ ]), respectively.<sup>10</sup> Such organization places the olefins in a position suitable for a UV-induced [2+2] cycloaddition reaction, as outlined by Schmidt.<sup>5</sup>

In line with the crystal structure of **1**, UV-irradiation (broadband Hg lamp) of a powdered sample of **1**, prepared by grinding **1** with a mortar and pestle,<sup>11</sup> produces *rc*tt-(2,4-tpcb-ht), as determined by  $^1\text{H}$  NMR spectroscopy, in quantitative yield.<sup>12,13</sup> To confirm the stereochemistry of the product, the photoreacted solid (0.318 g) was suspended in water (20 mL) and treated with NaOH until the suspension was basic to litmus (pH = 7–8).<sup>4</sup> The photoproduct was then extracted with chloroform (3 $\times$ 15 mL) and recovered as a white solid using a rotary evaporator. Single crystals of *rc*tt-(2,4-tpcb-ht) $\cdot$ 1.5(H<sub>2</sub>O) **2** were grown by dissolving the photoproduct (0.015 g) in chloroform (5 mL) and allowing the solution to slowly evaporate for a period of one day.<sup>14</sup>

A view of the X-ray crystal structure of **2** is shown in Fig. 2. Consistent with **1**, the photoproduct, two of which lie in the asymmetric unit and each of which sits around a crystallographic center of inversion, consists of a cyclobutane ring with two 2-pyridyl and two 4-pyridyl units in a ‘head-to-tail’ configuration. In a similar way to *rc*tt-(4,4-tpcb),<sup>2</sup> each pyridyl group is twisted out of the plane of each cyclobutane ring, the best planes of the pyridyl units based on N1 (C6,C7),

N2 (C6,C7), N3 (C18,C19), and N4 (C18,C19) being rotated by approximately 41.6(2), 83.6(1), 83.6(1), and 50.7(2) $^{\circ}$  with respect to the best planes of each cyclobutane unit, respectively. Notably, the tetrapyrindine has crystallized with 1.5 equivalents of water that self-assemble as linear trimers<sup>15</sup> held together by O–H $\cdots$ O hydrogen bonds [O $\cdots$ O separations (Å): O(1) $\cdots$ O(2) 2.748(4), O(1) $\cdots$ O(3) 2.781(4) Å] (Fig. 2b). In this

arrangement, the trimers bridge nearest-neighbor molecules of *rectt*-(2,4-tpcb-ht), by way of O–H $\cdots$ N forces involving the pyridyl units (Fig. 2a), such that the hydrogen bonds involving the 2-pyridyl groups [O $\cdots$ N separations (Å): O(1) $\cdots$ N(2) 2.895(4), O(2) $\cdots$ N(4) 2.857(3)] give rise to 1D columnar arrays along the crystallographic *a*-axis (Fig. 2b). The 1D arrays are cross-linked, by way of the hydrogen bonds involving



**Figure 2.** Perspectives of the X-ray crystal structure of **2**: (a) interaction between *rectt*-(2,4-tpcb-ht) and the linear water trimer (symmetry operations: *v*: 1–*x*, –*y*, –*z*; *vi*: –*x*, –*y*, –*z*), (b) 1D columnar array, and (c) the 3-D network structure along the crystallographic *a*-axis. Selected interatomic distances (Å): O(1) $\cdots$ O(2) 2.748(4), O(1) $\cdots$ O(3) 2.781(4), O(1) $\cdots$ N(2) 2.895(4), O(2) $\cdots$ N(4) 2.857(3).

the 4-pyridyl units [O $\cdots$ N separations (Å): O(3) $\cdots$ N(1)<sup>vii</sup> 2.879(3), O(2) $\cdots$ N(3)<sup>viii</sup> 2.795(3)] (symmetry operations: vii: 1-x, 1-y, -z; viii: x, 1/2-y, 1/2+z), to give a 3-D network structure (Fig. 2c).

In this report, we have demonstrated the ability of a multi-component solid based on cat to provide regio-controlled access to a functionalized head-to-tail cyclobutane — *rctt*-(2,4-tpcb-ht) — in quantitative yield. The components of the multi-component solid organize by way of a combination of O-H $\cdots$ N and O-H $\cdots$ O hydrogen bonds wherein the ability of the solid state to provide access to the product has been realized by way of crystal engineering approach to molecular solid-state synthesis.<sup>1,2</sup> Efforts are underway to utilize the photoproduct as a building block for the construction of metal-organic coordination arrays.<sup>3,4</sup> It is noted that similar crystalline solids, based on bifunctional molecules such as cat, may also be used to provide access to products difficult, or impossible, to achieve from solution.

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7. Crystal data for **1**: monoclinic, P 2<sub>1</sub>/c, *a*=7.487(2) Å, *b*=19.047(4) Å, *c*=11.047(2) Å,  $\beta$ =92.97(3)°, *U*=1573.3(3) Å<sup>3</sup>,  $2\theta$ =55°, MoK $\alpha$  radiation ( $\lambda$ =0.71070 Å) for *Z*=4 and *R*=0.033.
8. The hydroxyl groups of free cat, in contrast to **1**, form an intramolecular hydrogen bond. See: Wunderlich, V. H.; Mootz, D. *Acta. Cryst.* **1971**, *B27*, 1684.
9. Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
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11. X-ray analysis of the finely ground powder confirms that the structure of the powder is representative of the single-crystal structure of **1**.
12. 2,4-bpe is photoactive as a pure solid and produces a mixture of 'head-to-head' and 'head-to-tail' products upon UV-irradiation (unpublished results).
13. That the head-to-tail photoproduct of 2,4-bpe forms in quantitative yield suggests that the photoreaction has occurred either within or between the double layers of **1**. See, Savion, Z.; Wenick, D.L. *J. Org. Chem.* **1993**, *58*, 2424.
14. Crystal data for **2**: monoclinic, P 2<sub>1</sub>/c, *a*=11.281(2) Å, *b*=11.300(2) Å, *c*=17.879(4) Å,  $\beta$ =107.64(3)°, *U*=2172(2) Å<sup>3</sup>,  $2\theta$ =50°, MoK $\alpha$  radiation ( $\lambda$ =0.71070 Å) for *Z*=4 and *R*=0.050.
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