

## Unusual [2 + 2] Topochemical Cycloadditions of 3-Cyano- and 4-Cyano-cinnamic Acids: Temperature Dependent Solid State Photochemical Reactions

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The seeming difference in the topochemical [2 + 2] photoreactivity of 3-cyanocinnamic acid **1** and 4-cyanocinnamic acid **2** is caused by differing degrees of ease of molecular motion in the crystals and the unreactive **1** becomes reactive when heated to 130 °C.

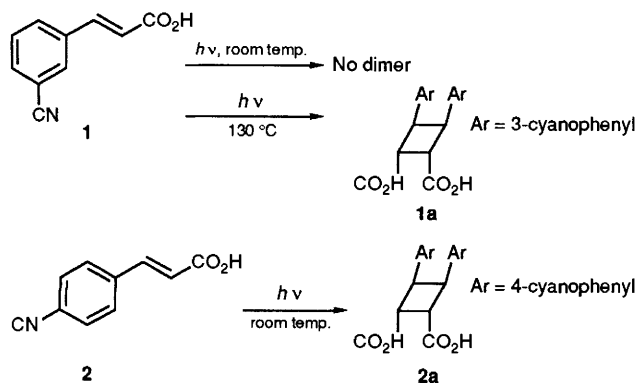
The literature on [2 + 2] topochemical cycloadditions has confirmed repeatedly that favourable double bond juxtaposition as measured by intermolecular geometry or by orbital overlap is the crucial factor in determining solid state reactivity.<sup>1-5</sup> This study was prompted by the observation that while the crystal structures of 3-cyanocinnamic acid, **1** and 4-cyanocinnamic acid, **2** are virtually identical with respect to the conventionally accepted criteria for solid state reactivity, that is, double bond centre-to-centre distance and  $\pi$ - $\pi$  overlap of the potentially reactive double bonds, only **2** was found to react topochemically on UV/sunlight irradiation. This observation raised at least two questions: (i) which is the unusual feature here: the photostability of **1** or the photoreactivity of **2**? (ii) why should these two identical crystal structures show drastically different reactivity patterns?

The crystal structures of acids **1** and **2** were solved,<sup>†</sup> both being  $\beta$ -structures<sup>1</sup> with the short axes  $\sim 4$  Å. The unit cell parameters and molecular packing (Figs. 1 and 2) show that these crystals may be termed isostructural. In both cases, the molecules are O-H...O hydrogen bonded **1**: O...O 2.60, H...O 1.56 Å; **2**: O...O 2.63, H...O 1.56 Å) to form centrosymmetrical dimers. The dimers, in turn are organised into molecular sheets utilising cyano...cyano dipole interactions (**1**: C...N 3.48 Å; **2**: C...N 3.47 Å) and weaker forces such as C-H...O (**1**: C...O 3.53, H...O 2.48 Å; **2**: C...O 3.54, H...O

2.49 Å) and C-H...N=C- (**1**: C...N 3.52, H...N 2.53 Å; **2**: C...N 3.49, H...N 2.54 Å). These molecular sheets are aligned along (-1 0 2) in **1** and (1 0 3) in **2**. In both cases, therefore, these planes are parallel to [0 1 0]. In acid **1**, the cyano groups are arranged in a 'zip like' fashion parallel to [0 1 0] while in **2** these dipole-dipole interactions are roughly along [0 0 1]. In both cases, C-H...O and C-H...N=C- interactions are very similarly aligned along the molecular sheets as shown in Figs. 1 and 2.

This close similarity in the crystal structures (and the sheet structures) of acids **1** and **2** suggested that molecular complex formation between these acids would be facile. In fact a mixed solution (MeCN or MeOH) containing 1 : 1 equivalents of **1** and **2**, yielded exclusively crystals of a 1 : 1 complex **3** (m.p. 216 °C). X-Ray powder spectra show that the crystal structure of **3** seems to resemble that of acid **1** much more closely than that of acid **2**, and also that complex **3** does not appear to be a solid solution of **1** and **2**.

When **1**, **2** and **3** were irradiated with UV/sunlight at ambient temperatures (25–35 °C), only **2** underwent a topochemical [2 + 2] photodimerisation reaction involving two [1 0 0] translated molecules to give the truxinic dimer **2a**§ in 94% yield [dimethyl ester of **2a**, m.p. 146 °C, IR (KBr)  $\nu/\text{cm}^{-1}$  3050, 2255, 1740, 840, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.5, 7.00 (dd, *J* 8 Hz, 8H), 4.48, 3.81 (AA'BB', *J*<sub>AB</sub> 7.07 Hz, 4H), 3.95 (s, 6H). MS (*m/z*, %) 374 M<sup>+</sup> (0.15), 230 (2.15%) (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>), 187 (89.3%) (M - C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub>), 173 (5%) (M - C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>), 172 (4%) (M - C<sub>12</sub>H<sub>12</sub>NO<sub>2</sub>), 156 (100%) (M - C<sub>12</sub>H<sub>12</sub>NO<sub>3</sub>), 144 (8%) (M - C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>), 128 (45%) (M - C<sub>13</sub>H<sub>12</sub>NO<sub>4</sub>)]. In contrast, **1** and **3** were found to be photostable. A close inspection of the two [1 0 0] translated molecules, in either **1** or **2**, shows that the overlap of potentially reactive double bonds is virtually the same in both structures (Figs. 1 and 2). Curiously, this overlap is not the most favourable for a topochemical cycloaddition reaction even though the double bond centre-to-centre distances are *ca.* 3.7–3.8 Å because



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‡ Crystal data for **1**: C<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>, *M* = 173, m.p. 236–238 °C, triclinic, space group P $\bar{1}$ , 163 K, *a* = 3.812(4), *b* = 7.891(5), *c* = 14.121(2) Å,  $\alpha$  = 81.42(8),  $\beta$  = 84.60(8),  $\gamma$  = 89.51(8)°, *V* = 418.1(7) Å<sup>3</sup>, *F*(000) = 180, *Z* = 2, *D*<sub>c</sub> = 1.37 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.58 cm<sup>-1</sup>, 390 independent reflections with *I* > 2 $\sigma$ (*I*). Crystal data for **2**: C<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>, *M* = 173, m.p. 255–256 °C, triclinic, space group P $\bar{1}$ , 153 K, *a* = 3.770(2), *b* = 7.703(5), *c* = 14.319(3) Å,  $\alpha$  = 89.09(5),  $\beta$  = 82.91(4),  $\gamma$  = 81.72(5)°, *V* = 408.3(4) Å<sup>3</sup>, *F*(000) = 180, *Z* = 2, *D*<sub>c</sub> = 1.41 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 1.01 cm<sup>-1</sup>, 936 independent reflections with *I* > 2 $\sigma$ (*I*). For both compounds, the data were collected on a R3m diffractometer. All computations were performed with SHELXTL, *R* = 0.085; *R*<sub>w</sub> = 0.042 (acid **1**); *R* = 0.043; *R*<sub>w</sub> = 0.041 (acid **2**); C, N, O anisotropic; H isotropic; 146 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

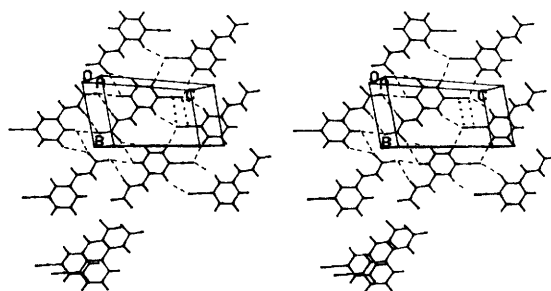


Fig. 1 A stereo diagram of a molecular sheet of acid **1**. The cyano...cyano dipole interactions are shown as dotted lines and C-H...O and C-H...N=C- interactions are marked as dashed lines. The overlap of [1 0 0] translated incipient photoreactive molecules are also shown.

§ The dimer acids **1a** and **2a** were esterified with CH<sub>2</sub>N<sub>2</sub> for easier separation and characterisation.

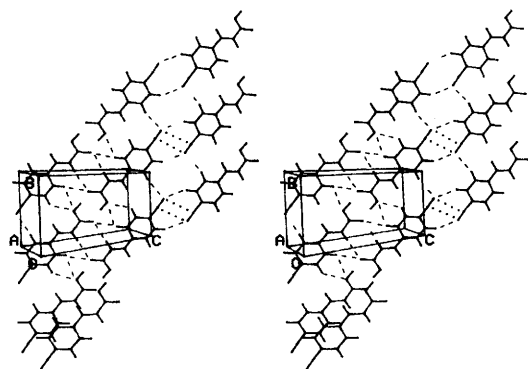


Fig. 2 A stereo diagram of a molecular sheet of acid 2 notated as in Fig. 1

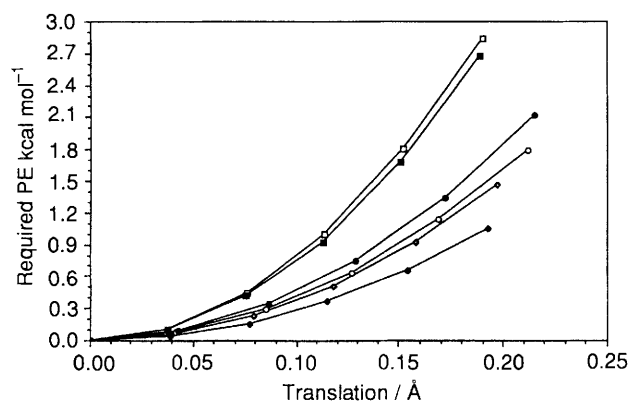


Fig. 3 Increase in the potential energy (PE) for acid 1 and acid 2 as a function of translational motion about the three crystal axes. A single molecular unit is translated in the constant field of its neighbours. □: 1 *a* axis translation; ◇: 1 *b* axis translation; ○: 1 *c* axis translation; ■: 2 *a* axis translation; ◆: 2 *b* axis translation; ●: 2 *c* axis translation.

of a large lateral offset of double bonds.<sup>4</sup> This observation suggests perhaps that the photoreactivity of 2 is unusual and not the photostability of 1.

To resolve this dilemma, packing potential energy calculations and molecular translational motion energy calculations were performed on 1.<sup>¶</sup> The hydrogen bonded dimers were considered as single molecular units for this analysis. The difference in the topochemical reactivity of 1 and 2 was interpreted in terms of the difference in the translational motion required to obtain optimal  $\pi$ - $\pi$  overlap between double bonds of incipient reactive molecules. Motion of a single molecular unit in 1 or 2 along [1 0 0] produced very similar potential curves shown in Fig. 3, indicating that a similar amount of energy is needed for the given translational motion in either case. Almost similar curves were obtained for motion along [0 0 1] also in both cases with the small difference being attributed to dipole-dipole interactions along

¶ OPEC, A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220. Mirsky potentials were used. All hydrogens were relocated at 1.08 Å from their respective carbon atoms and were used in calculations. Electrostatic interactions were included explicitly. The partial atomic charges were assigned from the semi-empirical molecular orbital calculations with MOPAC using AM1 parameters. The object of these calculations was not to obtain absolute crystal energies but to establish differences in energy between alternative, slightly displaced molecular positions. These energy differences are quite insensitive to the actual potentials used.

[0 0 1] in acid 2. However, motion along [0 1 0] is easier compared with the two other motions in both cases. Further and more significantly, this [0 1 0] motion is easier in acid 2 when compared to acid 1 as seen by the shallow potential curve (◆ in Fig. 3). Perhaps motion along [0 1 0] is more difficult in acid 1 because of the compact 'zip like' arrangement of cyano groups. This translational motion along [0 1 0] is essential for better overlap of the  $\pi$ -orbitals of the nearest double bonds and therefore necessary for reactivity. The photostability of acid 1 is thus explained. At this stage and upon inspection of Fig. 3, it was felt that if crystalline 1 were heated during irradiation, reaction would ensue (assuming no phase transition on heating).<sup>||</sup> Conversely, cooling a sample of crystalline 2 during irradiation should suppress its solid state reactivity.

These predictions were confirmed exactly. Acid 1 *did* undergo dimerisation on sunlight irradiation while heating to 130 °C and forms the truxinic dimer 1a in 80% yield [dimethyl ester of 1a, m.p. 138 °C, IR (KBr)  $\nu/\text{cm}^{-1}$  3250–2750, 2250, 1690, 1240, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.35–7.10 (m, 8H), 4.38, 3.72 (AA'BB', *J*<sub>AB</sub> 8.8 Hz, 4H), 3.68 (s, 6H), MS (*m/z*, %) 230 (5%) (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>), 187 (50%) (M - C<sub>11</sub>H<sub>9</sub>NO<sub>2</sub>), 173 (100%) (M - C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>), 172 (85%) (M - C<sub>12</sub>H<sub>12</sub>NO<sub>2</sub>), 156 (60%) (M - C<sub>12</sub>H<sub>12</sub>NO<sub>3</sub>), 144 (6%) (M - C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>), 128 (40%) (M - C<sub>13</sub>H<sub>12</sub>NO<sub>4</sub>). Further, the yield of dimer 2a decreased from 94% at 30 °C to 72% at 0 °C to essentially 0% at -80 °C. Differential scanning calorimetry (DSC) measurements on 1 showed no phase change up to the melting point. X-Ray diffraction studies on a single crystal of 2 indicated no phase change from -120 °C to room temperature. Preliminary studies on complex 3 showed that there is no photoreactivity even while heating up to 130 °C. Lastly, neither 1 nor 3 showed any reactivity on heating to 130 °C in the dark, indicating that the photoreactivity of 1 is thermally induced. Further heating of 3 to higher temperatures led to melting, and no photoreactivity was observed. More work on this aspect is in progress.

While there has been a report on the effects of thermal energy on the efficiency of photochemical [2 + 2] solid state cycloaddition reactions,<sup>6</sup> we believe this to be a novel example of a photostable material which becomes photoactive upon heating. In addition to practical applicability, our results are interesting because it may become necessary to reexamine older compounds which have been classified as being 'unreactive' in the solid state using topochemical and other criteria.

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|| Fig. 3 shows that at ~130 °C, acid 1 has the same amount of molecular translational motion along [0 1 0] as does acid 2 at room temperature (27 °C).