Stepwise Dimerization of Double [2+2] reaction in the Co-crystals of 1,5-bis(4-pyridyl)-1,4-pentadiene-3-one and Phloroglucinol: A Single Crystal to Single Crystal Transformation

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Supporting Information (8 pages)

(synthesis details, NMR-assignment, Hydrogen bonding details and NMR spectra)
**Crystallization of 2:**
A (1:1) mixture of resorcinol (0.020g) and 1 (0.0436g) were dissolved in ethyl acetate (7ml.) and left for crystallization. Brownish crystals of 2 were formed after 36 hours in 75% yield. The crystallization with many other solvents or solvent mixtures such as acetone, acetonitrile benzene-THF, toluene-acetonitrile resulted in similar type of co-crystals. The similarity of these crystals has been identified by determining the unit cell parameters and melting points (185°C-190°C).

**Crystallization of 3:**
A 1:1 mixture of 1 (.05g, .212mmol) and phloroglucinol, 2H2O (.0343g) was dissolved in 15ml of acetonitrile and left at rt. in dark. Light yellow rod like crystal were obtained in 69%. (.0584g) yield in 12 hour. mp: single crystal started to loose solvent above 75°C then melting started at 185-190°C with gradual blackening and no clear melting up to 300°C. 1H NMR: (400 MHz. D6DMSO) δ 2.057 (s; 3H, acetonitrile proton); δ 5.634 (s; 3H, phloroglucinol-OH); δ 7.559 (d; J = 16 Hz; 2H, alkene proton β to Py); δ 7.730 (d; J = 5.2 Hz; 4H, Py-βH); δ 7.778 (d; J = 16 Hz; 2H, alkene proton α to Py); δ 8.668 (d; J = 5.2 Hz; 4H, Py-αH); δ 8.925 (s; 3H, phloroglucinol phenyl proton).

**Preparation of 4:**
Crystals, after separation from crystallization solvent, were directly exposed under sunlight or uv-light (medium pressure Hg vapour lamp:350-420 nm) putting on watch-glass. Larger crystals started to changing white in colour with disintegrating into smaller fragments while smaller crystal remain intact and 100% reaction occurred in 3-4 hours or 15 minute in sunlight or uv-light respectively (checked by TLC). 1H NMR: (400 MHz. D6DMSO) δ 2.057 (s; 6H); δ 4.429 (d; J = 5.6 Hz; 4H, Cy-butane proton β to Py); δ 4.642 (d; J = 5.6 Hz; 4H, Cy-butane proton α to Py); δ 5.633 (s; 6H) δ 7.080 (d; J = 5.6 Hz; 8H, Py-βH); δ 8.293 (d; J = 5.6 Hz; 8H, Py-αH); δ 8.928 (s; 6H).
Separation of TCD from 4:
About 1g of 100% photolized product 3 was dissolved in 50 ml water by adding 1N HCl solution dropwise (until all material dissolved). The yellow coloured solution was extracted with 50 ml ethyl acetate 3-4 times. The aqueous part was then neutralized by dropwise addition of dilute aqueous tri-ethylamine solution. The white precipitation obtained was filtered and washed with water and dried. The dimer TCD obtained in quantitative yield were recrystalized from THF as a white crystals. mp: 210-215°C.

Generation of partially reacted material of 3 & the spectral proof for stepwise formation of TCD:
A partially reacted 3 in which TCD is in 40-60% in mole ratio can be generated by irradiating crystals directly either in sunlight for 2 hours or in UV light for 6 minutes putting on watch glass.

For monitoring the photolysis reaction of 3 by $^1$HNMR spectra the light(hV) source used was room light i.e. of low intensity. From this study and also from the $^1$HNMR spectra for that irradiated 2 hours in sunlight we characterized a full set of peak position for the product of single (2+2) reaction (scheme-1): $^1$H NMR: (400 MHz. D$_6$DMSO) $\delta$ 4.295 (d; $J = 6$ Hz; 2H, Cy-butane proton $\beta$ to Py); $\delta$ 4.784 (d; $J = 6$ Hz; 2H, Cy-butane proton $\alpha$ to Py), $\delta$ 7.121 (d; $J = 16$ Hz; 2H, alkene proton $\beta$ to Py); $\delta$ 7.159 (d; $J = 5.6$ Hz; 4H, Py- $\beta$H attach to Cy-butane); $\delta$ 7.542 (d; $J = 5.6$ Hz; 4H, Py- $\beta$H attach to alkene); $\delta$ 7.554 (d; $J = 16$ Hz; 2H, alkene proton $\alpha$ to Py); $\delta$ 8.316 (d; $J = 5.6$ Hz; 4H, Py- $\alpha$H attach to Cy-butane); $\delta$ 8.533 (d; $J = 5.6$ Hz; 4H, Py- $\alpha$H attach to alkene). Table 1 shows the significant shift in $\delta$ value for that 1, dimer I and the product of single (2+2) reaction.
Scheme-1: Product of single (2+2) reaction.
TABLE 1: Showing different ¹H NMR Position (δ  value).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Py-α H Attach To Cy-butane</th>
<th>Py-β H Attach To Cy-butane</th>
<th>Py-α H Attach to alkene</th>
<th>Py-β H Attach to alkene</th>
<th>Alkene Proton α-to Py</th>
<th>Alkene Proton α-to keto</th>
<th>Butane Proton α-to Py</th>
<th>Butane Proton α-to keto</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant 1</td>
<td>8.668</td>
<td>7.730</td>
<td>7.778</td>
<td>7.559</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single (2+2) Pdt.</td>
<td>8.316</td>
<td>7.159</td>
<td>8.533</td>
<td>7.542</td>
<td>7.554</td>
<td>7.121</td>
<td>4.784</td>
<td>4.295</td>
</tr>
<tr>
<td>Double (2+2) Pdt.</td>
<td>8.293</td>
<td>7.080</td>
<td>4.642</td>
<td>4.429</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crystal data for 1 (C₁₅H₁₂N₂O₁): M=236.27, Monoclinic, P2(1)/n, a= 8.1243(4) Å, b= 15.3477(7) Å, c= 10.0546(4) Å, β= 104.0370(10)°, V= 1216.26(9) Å³, Z = 4; 2089 reflections out of 2932 unique reflections with I > 2σ(I), 2.47<θ<28.00°, final R₁ = 0.0441, wR₂ = 0.1266.

Crystal data for 2: (C₂₁H₁₈N₂O₃): M=346.37, Monoclinic, P2(1)/c, a= 9.543(4) Å, b= 21.387(9) Å, c= 8.802(4) Å, β= 94.868(13)°, V= 1790.0(13) Å³, Z = 4; 2520 reflections out of 3912 unique reflections with I > 2σ(I), 1.90<θ<27.16°, final R₁ = 0.0427, wR₂ = 0.1155.

Hydrogen Bonding parameter for 2
O2A -- H2AO .. N11 [ 4754.01] 1.829(19) 2.753(2) 174.4(17)
O1A -- H1AO .. N21 [ ] 1.87(3) 2.759(2) 161(3)
C5 -- H5 .. O2A [ 4454.02] 2.55 3.205(2) 127
C15 -- H15 .. O2A [ 2445.02] 2.60 3.319(3) 135

Translation of ARU-code to Equivalent Position Code
===============================================
[ 4454. ] = -1+x, 1/2-y, -1/2+z
[ 2445. ] = -1-x, -1/2+y, 1/2-z
[ 4754. ] = 2+x, 1/2-y, -1/2+z

Hydrogen Bonding parameter for 3
O(1) -- H(10) .. N(21) [ 3565.01] 1.86(4) 2.761(3) 177(3)
O(3) -- H(30) .. N(31) [ 4464.01] 1.94(3) 2.803(3) 171(3)
O(5) -- H(50) .. N(100) [ ] 2.03(3) 2.828(3) 162(3)
C(11) -- H(11) .. O(5) [ 5555.02] 2.55 3.350(3) 145
O(3) ---- C(101) [ ] 7555.03 3.202(3) < 3.22 -0.02

Hydrogen Bonding parameter for 4
O1A -- H1AO .. N100 [ 3656.03] 1.92(6) 2.811(7) 153(5)
O3A -- H3AO .. N11 [ 4564.01] 1.78(6) 2.747(6) 173(5)
O2A -- H2AO .. N21 [ 4564.01] 1.75(8) 2.773(6) 169(7)
C2 -- H2 .. O1A [ 5555.02] 2.47 3.323(7) 145
C101 -- H10A .. O3A [ 5545.02] 2.55 3.420(7) 151

Electronic Supplementary Material (ESI) for CrystEngComm
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Translation of ARU-code to Equivalent Position Code

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[ 2756. ] = 2-x, y, 3/2-z
[ 4564. ] = x, 1-y, -1/2+z
[ 5555. ] = 1/2+x, 1/2+y, z
[ 3656. ] = 1-x, -y, 1-z
[ 5545. ] = 1/2+x, -1/2+y, z

Hydrogen Bonding parameters for 5.

O1A -- H1AO .. N21 [          ]  1.80(4)  2.755(4)  170(3)
O3A -- H3AO .. N11 [ 2756.01]  1.76(4)  2.765(4)  176(3)
O2A -- H2AO .. N100 [          ]  1.94(5)  2.810(5)  164(4)
C2' -->H2' .. O2A [ 7656.02 2.47  3.352(11)     149
H10A .... O3A [ 7556.02]  2.6604 < 2.72 -0.06
     0.0617  0.1034  0.3480  0.0113  0.1843  0.4603
     C101      138.06
O3A .... C101 [ 5455.03]  3.420(7)  3.22  0.20
     0.4917  0.3097  0.4587  0.4031  0.3782  0.3105  C5A  160.8(3)

Translation of ARU-code to Equivalent Position Code

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[ 2756. ] = 2-x, y, 3/2-z
[ 7656. ] = 3/2-x, 1/2-y, 1-z
$^1$HNMR spectra of 3.

$^1$HNMR spectra of 4.
$^1$HNMR spectra of partially irradiated 3 in sunlight for 2 hours.

$^1$HNMR spectra of 3 after 2 days irradiation in room light.
$^1$HNMR spectra of 3 after 4 days irradiation in room light.

$^1$HNMR spectra of 3 after 15 days irradiation in room light.