Electronic Supplementary Material (ESI) for CrystEngComm

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 1:1mixture of 1(.05g, .212mmol) and phloroglucinol, $2H_2O$(.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. ^{1}H NMR: (400 MHz. D_6DMSO) 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). ^{1}H NMR: (400 MHz. D_6DMSO) 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).

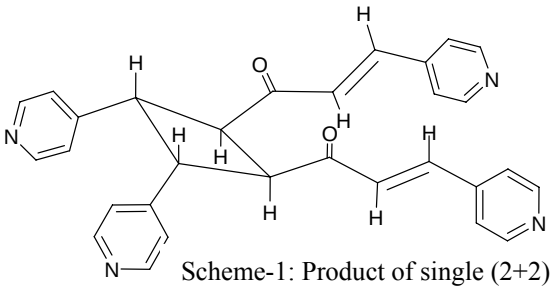
Separation of TCD from 4:

About 1g of 100% photolized product **3** was dissoldved in 50 ml water by adding1N HCl solution dropwise (until all material dissolved). The yellow coloured solution was extracted with 50 ml ethyl acetate 3-4 times. The aquous part was then neutralized by dropwise addition of dilute aquous 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($h\nu$) 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_6DMSO) δ 4.295 (d; *J* = 6 Hz; 2H, Cy-butane proton β to Py); δ 4.784 (d; *J* = 6 Hz; 2H, Cy-butane proton α to Py), δ 7.121 (d; *J* = 16 Hz; 2H, alkene proton β to Py); δ 7.159 (d; *J* = 5.6 Hz; 4H, Py- βH attach to Cy-butane); δ 7.542 (d; *J* = 5.6 Hz; 4H, Py- βH attach to alkene); δ 7.554 (d; *J* = 16 Hz; 2H, alkene proton α to Py); δ 8.316 (d; *J* = 5.6 Hz; 4H, Py- αH attach to Cy-butane); δ 8.533 (d; *J* = 5.6 Hz; 4H, Py- αH attach to alkene).Table.**1** shows the significant shift in δ 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 ^{1}HNMR Position (δ value).

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

Crystal data for **1** ($C_{15}H_{12}N_2O_1$): *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)º, V= 1216.26(9) Å^3, *Z* = 4; 2089 reflections out of 2932 unique reflections with I > 2σ(I), 2.47<θ<28.00°, final R_1 = 0.0441, wR_2 = 0.1266.

Crystal data for **2**: ($C_{21}H_{18}N_2O_3$): *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)º, V= 1790.0(13) Å^3, *Z* = 4; 2520 reflections out of 3912 unique reflections with I > 2σ(I), 1.90<θ<27.16°, final R_1 = 0.0427, wR_2 = 0.1155.

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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(1O) .. N(21) [  3565.01]  1.86(4)   2.761(3)     177(3)
O(3)  -- H(3O) .. N(31) [  4464.01]  1.94(3)   2.803(3)     171(3)
O(5)  -- H(5O) .. 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
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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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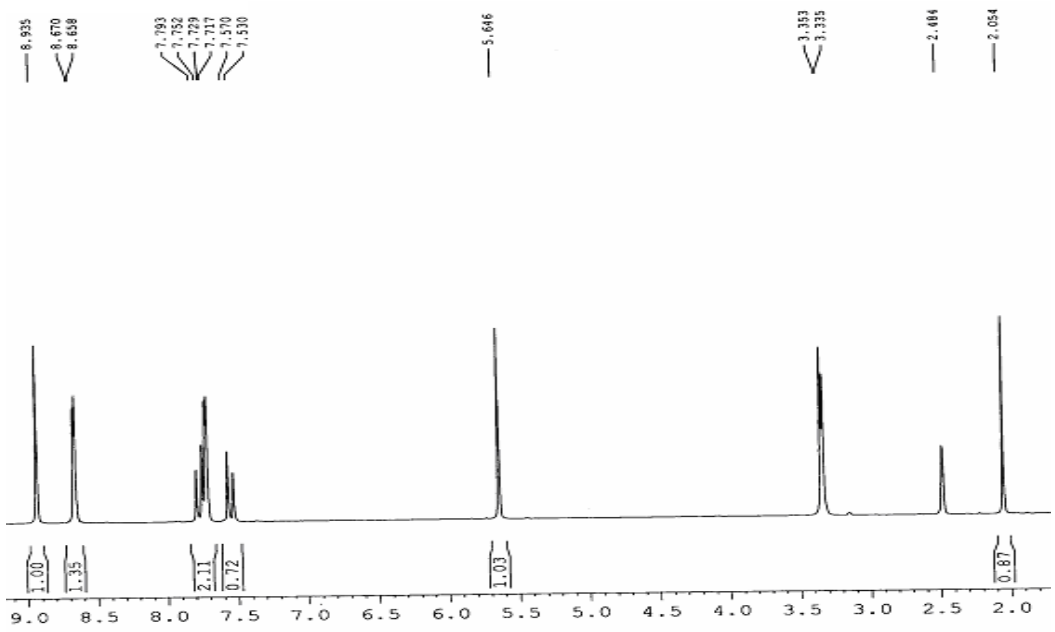
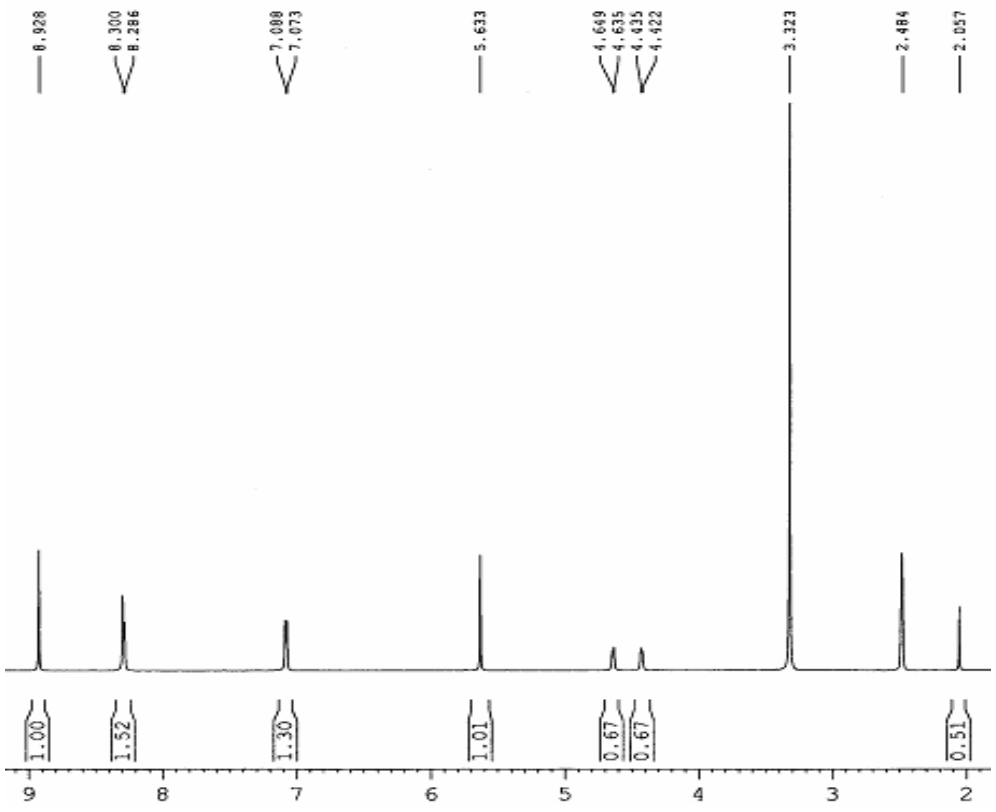
   [  7656. ]  = 3/2-x,1/2-y,1-z
```

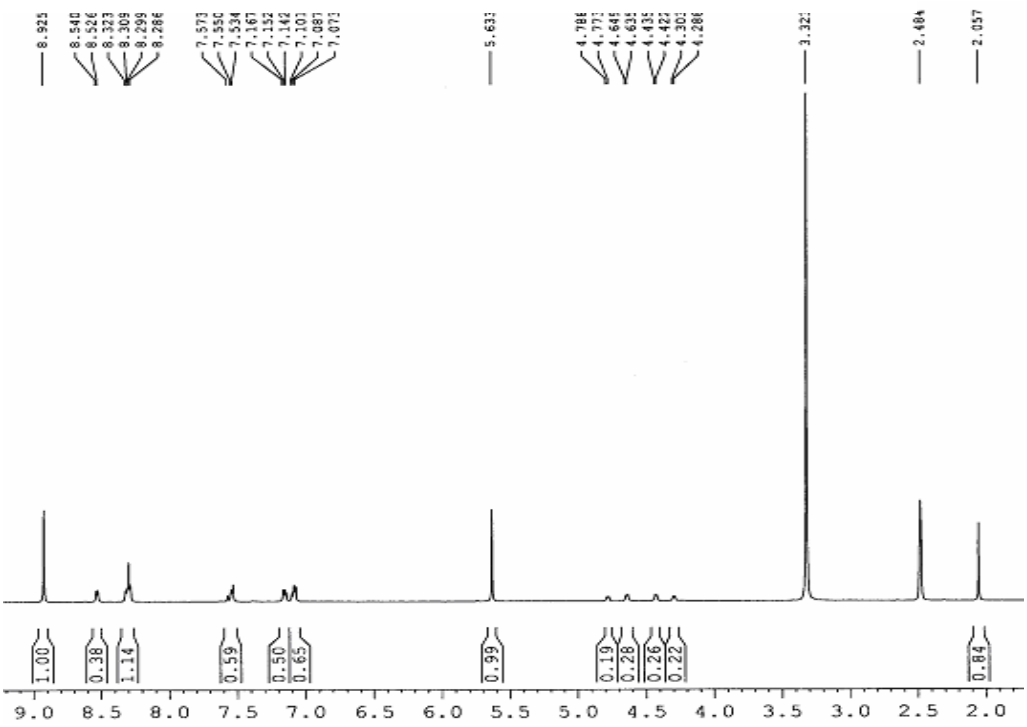
[1]HNMR spectra of **3.**



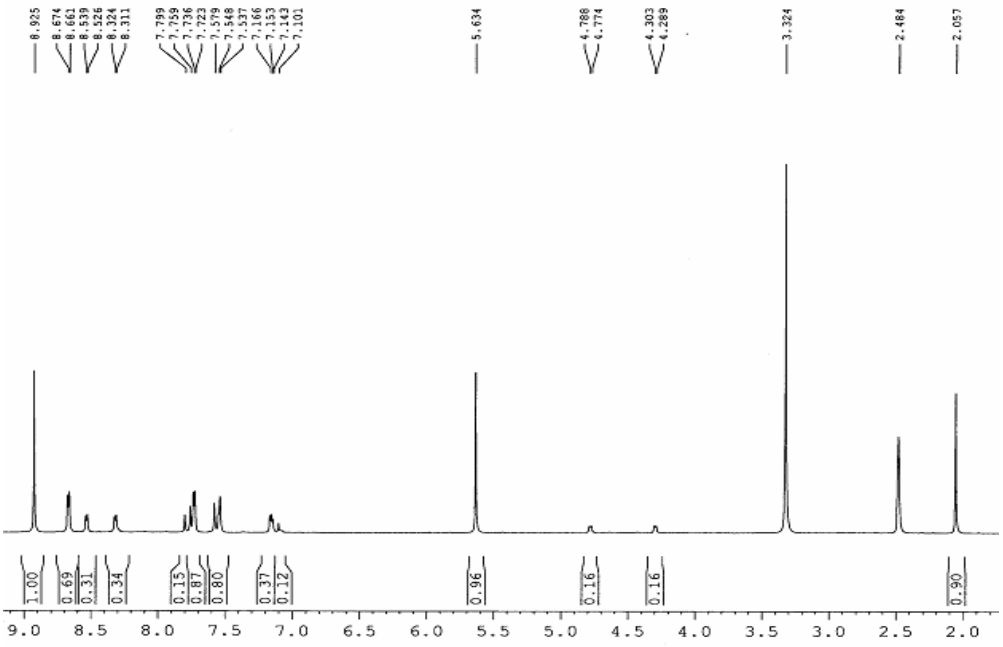
[1]HNMR spectra of **4.**



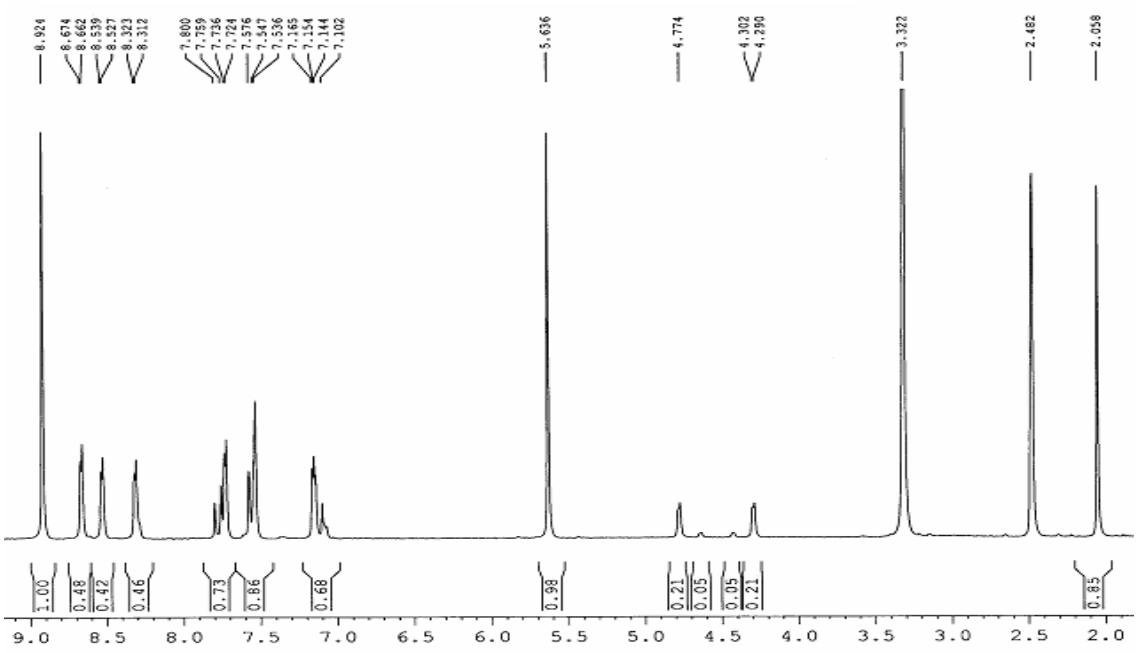
[1]HNMR spectra of partially irradiated **3** in sunlight for 2 hours.



[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.