

Hydrogen-bond quenching of photodecarbonylation in the solid state and recovery of reactivity by crystal engineering

Jing Zhang, Milan Gembicky, Marc Messerschmidt, Philip Coppens

*Department of Chemistry, State University of New York at Buffalo, Buffalo,
New York, 14260-3000, USA. E-mail: coppens@buffalo.edu;*

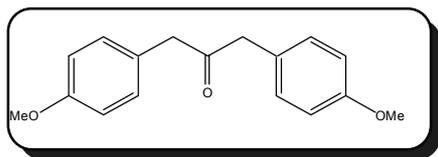
Fax: (716)645-6948

Supporting Information

All starting materials were purchased from commercial sources and used as received unless stated otherwise.

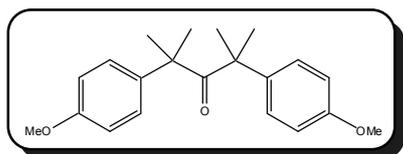
¹H (500 MHz) spectra were recorded on Varian Inova-500 (broadband) spectrometers or Varian Inova-400 (broadband) spectrometers. Chemical shifts (in ppm) are given relative to non-deuterated DMSO. UV/Vis spectra were recorded on a Perkin-Lambda 35 UV/Vis spectrophotometer. Steady-state excitation and emission spectra were obtained on SPEX 1681 Fluorolog-2 series F111AI or SPEX Fluorolog-3 spectrophotometers. IR spectra were collected on a Perkin Elmer 1760 Infrared spectrometer. Melting points were determined either on a by a Perkin-Elmer DSC-7/TGA-7 in a conventional melting point tube. Room temperature irradiation of powdered crystalline samples was carried out with a 100W Oriel Mercury Arc Lamp. For low temperature irradiation of single crystals a 325nm Helium Cadmium laser system (40mW) was used. Elemental analysis was

performed by Department of Inorganic Chemistry, of the Slovak Technical University, Bratislava, Slovakia.



Bis(4-methoxybenzyl) ketone was synthesized

according to a slightly modified known procedure.¹ *p*-Methoxyphenylacetic acid (16.6g, 100 mmol) was ground with BaCO₃ (30g 150mmol). The mixture was then intensively stirred at 140°C without solvent for 4h until gas evolution ceased. The resulting solid was ground and dried under vacuum. The product was distilled off under vacuum and purified by recrystallization from diethyl ether to eliminate the side product 4-methoxybenzeneacetic acid methyl ester (yield 40%). Yield 33%. ¹HNMR (500 MHz, CDCl₃) δ = 3.64 (s, 4H, α-hydrogen), 3.80 (s, 6H, *p*-methoxy), 6.85 (d, 4H, ³J_{HH} = 8.5 Hz, aryl H), 7.05 (d, 4H, ³J_{HH} = 8.5 Hz, aryl H)



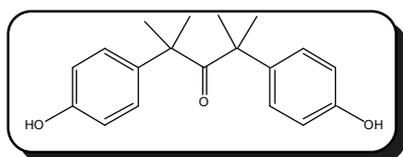
2, 2, 4, 4-Tetramethyl -1,3 di(4-methoxyphenyl)acetone

was prepared from bis(4-methoxybenzyl) ketone according to reference 2. The pure compound was obtained by recrystallization from ethanol in a yield of 90%. ¹H NMR (500 MHz, CDCl₃,) : δ = 1.27 (s, 12H, α-methyl), 3.80 (s, 6H, *p*-methoxy), 6.78 (d, 4H, ³J_{HH} = 8.5 Hz, aryl H), 7.07 (d, 4H, ³J_{HH} = 8.5 Hz, aryl H). IR (KBr cm⁻¹): 2970, 1683,

1 R. Ruzicka, L. Baráková, P. Klán, *J. Phys. Chem. B* **2005**, *109*, 9346-9353.

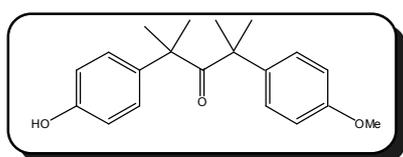
2 M. J. E. Resendiz, M. A. Garcia-Garibay, *Org. Lett.* **2005**, *7*, 371-374

1608, 1580, 1511, 1465, 1298, 1253, 1187, 1032, 995, 826, 810, 585, 542. HRMS (ESI) m/z (M^+) calcd for $C_{21}H_{26}O_3Na$ [$M+Na$] $^+$, 349.1774, found 349.1767.



2, 2, 4, 4-Tetramethyl -1,3 di(4-hydroxyphenyl)acetone 1

was prepared by demethylation of *2, 2, 4, 4-Tetramethyl -1,3 di(4-methoxyphenyl)acetone* (1g) in molten pyridine hydrochloride (10g) at 200°C for 2h. The resulting warm mixture was poured into ice water. A white powder was collected by filtration and recrystallized from chloroform for purification. Yield 88%. 1H NMR (400 MHz, d^6 -DMSO, δ): δ =1.16 (s, 12H, α -methyl), 6.68 (d, 4H, $^3J_{HH}$ = 8.4 Hz, aryl H), 6.95 (d, 4H, $^3J_{HH}$ = 8.5 Hz, aryl H), 9.34 (s, hydroxyl). IR (KBr cm^{-1}): 3360, 2970, 1659, 1611, 1595, 1513, 1475, 1451, 1271, 1239, 1181, 1032, 993, 906, 827, 689, 588, 532. HRMS (EI) m/z (M^+) calcd for $C_{19}H_{22}O_3$, 298.15634, found 298.15650. Melting Point 180°.



2, 2, 4, 4-tetramethyl -1-(4-hydroxyphenyl)-3-(4-

methoxyphenyl)acetone 2. 300mg(1mmol) of **1** and 162mg (0.5mmol) Cs_2CO_3 in 20mL acetone was stirred for 4h and then MeI(560mg 4mmol) in 5mL acetone was added dropwise. The reaction mixture was stirred overnight, water was added, followed by extraction with diethyl ether. The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure. Pure compound **2** was obtained by column chromatography, [silica, ether (20%)/hexanes (80%)]. Colorless crystals were obtained from the same

solvent mixture. Yield 45%. $^1\text{H NMR}$ (400 MHz, $\text{d}^6\text{-DMSO}$,): δ = 1.15 (s, 6H, α -methyl H), 1.17 (s, 6H, α' -methyl H), 3.73 (s, 3H, *p*-methyoxyl H), 6.67 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 6.84 (d, 2H, $^3J_{\text{HH}} = 9$ Hz, aryl H), 6.93 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 7.06 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 9.32 (s, hydroxyl H). IR (KBr cm^{-1}): 3257, 2971, 1679, 1610, 1512, 1460, 1294, 1254, 1186, 1035, 994, 831, 588, 541. HRMS (EI) m/z (M^+) calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3$, 312.17199, found 312.17192. Melting Point: 83-85.

Synthesis and characterization of 1a: To a solution of **1** (30mg 1mmol) in 10mL ether, 4,4'-biscyclohexanone (20mg 1mmol) was added. The resultant solution mixture was stirred at room temperature for 0.5h after which 20mL *n* hexane was added and the resulting solution was filtered. After overnight evaporation colorless crystals appeared.

Yield: 40%. $^1\text{H NMR}$ (500 MHz, $\text{d}^6\text{-DMSO}$,): δ = 1.14 (s, 12H, α -methyl), 1.41-1.47 (m, 4H), 1.68-1.72(m, 2H), 1.96-2.00 (m, 4H), 2.18-2.21(m, 4H), 2.34-2.41(m, 4H), 6.67 (d, 4H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 6.94 (d, 4H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 9.31 (s, hydroxyl). IR (KBr cm^{-1}): 3254, 2968, 1685, 1611, 1593, 1509, 1472, 1265, 1231, 1180, 1032, 993, 836, 585, 543. Elemental analysis calc. for $\text{C}_{31}\text{H}_{40}\text{O}_5$: C 75.57, H 8.19; found C 75.95, H 8.63.

Synthesis and characterization of 2a: To a solution of **2** (32mg 1mmol) in 10mL ether, 4, 4'-biscyclohexanone (10mg 0.5mmol) was added. The resultant solution mixture was stirred at room temperature 0.5h and then 20mL *n*hexane was added. The solution was filtered. After overnight evaporation the colorless crystals appeared in the bottom of beaker. Yield: 80%. $^1\text{H NMR}$ (500 MHz, $\text{d}^6\text{-DMSO}$,): δ = 1.15 (s, 6H, α -methyl H), 1.17 (s, 6H, α' -methyl H), 1.42-1.47 (m, 2H), 1.68-1.71(m, 1H), 1.96-2.00 (m, 2H), 2.18-

2.22(m, 2H), 2.34-2.42(m, 2H), 3.73 (s, 3H, *p*-methyoxyl H), 6.67 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 6.84 (d, 2H, $^3J_{\text{HH}} = 9$ Hz, aryl H), 6.93 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 7.06 (d, 2H, $^3J_{\text{HH}} = 8.5$ Hz, aryl H), 9.32 (s, hydroxyl H). IR (KBr cm^{-1}): 3263, 2971, 1698, 1685, 1613, 1590, 1513, 1461, 1255, 1232, 1185, 1031, 994, 825, 583, 543. Elemental analysis calc. for $\text{C}_{52}\text{H}_{62}\text{O}_4 \cdot \text{H}_2\text{O}$: C 74.96, H 7.75; found C 74.97, H 8.13.

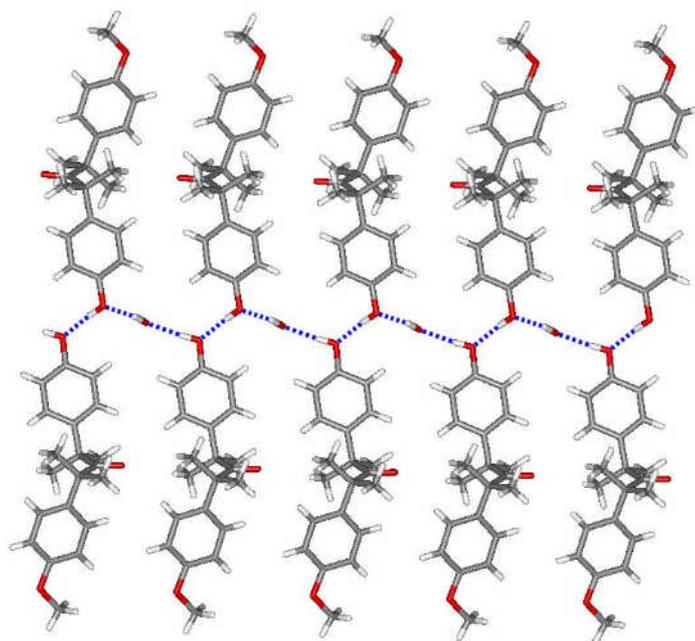


Fig. S1. Hydrogen bonding in **2** Intermolecular hydrogen bond distances (Å): O2...O5A
2.75, O5...O7 (water) 2.60, O2...O7 (water) 2.71

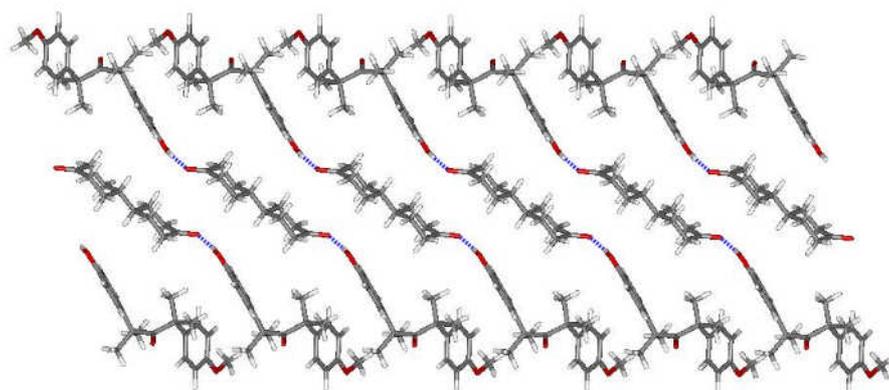


Fig. S2. Hydrogen bonding in **2** Intermolecular hydrogen bond distances (Å): O3...O4
2.72

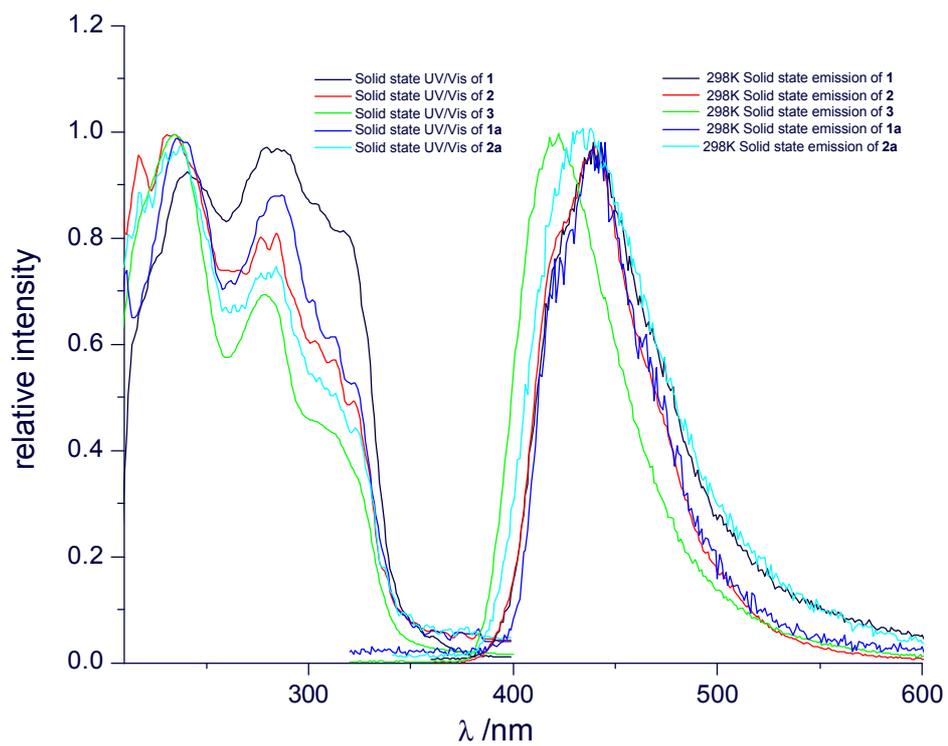


Fig. S3. Solid state UV/Vis absorption spectra and solid state emission of **1**, **2**, **3**, **1a** and **2a** at 298K. Excitation wavelength 350nm

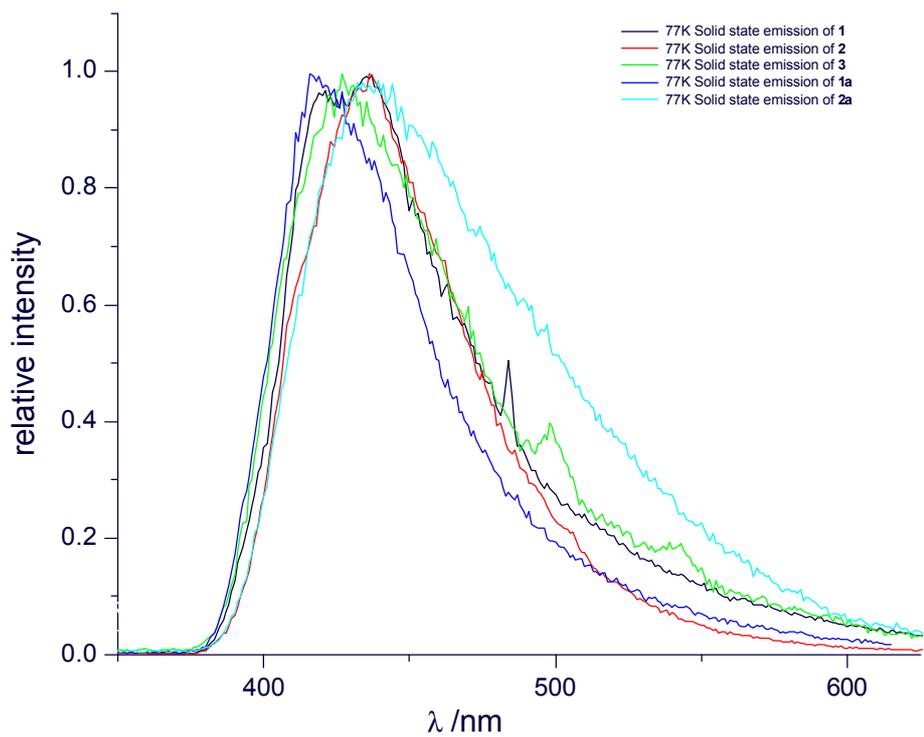


Fig. S4. Solid state emission of **1**, **2**, **3**, **1a** and **2a** at 77K, excitation wavelength 350nm

Compound name	D-H	A	Hydrogen bond distance D...A (Å)
1	O2-H2A	O3 (hydroxyl-)	2.771
	O3-H3A	O1 (carbonyl)	2.718
2	O2-H2A	O5 (carbonyl)	2.754
	O5-H5A	O7 (water)	2.595
	O7-H7D	O2 (carbonyl)	2.707
1a	O2-H2A	O4 (carbonyl from template)	2.760
	O3-H3A	O5 (carbonyl from template)	2.735
2a	O3-H3A	O4 (carbonyl from template)	2.719

Table S1. Hydrogen bonding in compounds 1, 2, 1a and 2a

Compound	Carbonyl Frequency (cm ⁻¹)
1	1659
2	1679
3	1683
1a	1685
2a	1698, 1682

Table S2. Carbonyl stretching frequencies for compounds 1, 2, 3, 1a and 2a.

	a (Å)	b	c	α (°)	β	γ
90K	7.7478(3)	11.0122(4)	16.6440(7)	109.248(1)	92.649(1)	90.731(1)
15min	7.7750(3)	11.0364(5)	16.6918(7)	109.3888(12)	93.1995(13)	90.5739(13)
20min	7.8085(5)	11.0256(7)	16.7261(11)	109.358 (2)	93.814 (2)	90.406 (2)

Table S3. Unit cell dimensions of 1a after different irradiation times with 325nm laser light.