SUPPLEMENTARY INFORMATION

Solid State Photochromism and Photoreactivity of *o*- and *p*-Anisaldehydes. Remarkable Stabilization of *o*-Xylylenols

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Photolysis Experiments. The powdered samples or crystals as such dispersed in a pyrex test tube were exposed to UV-vis light in a Rayonet reactor fitted with UV lamps (λ = 350 nm) or High Pressure Hg lamp (200 W, Applied Photophysics). All anisaldehydes **1b-c**, **2c** and **3** with the exception of **2b** turned brick-red color instantaneously. ^{1}H NMR (400 MHz) analysis of **1c** after prolonged irradiation in the Rayonet reactor indicated predominantly the starting material with its cyclobutenol barely observable (<5%). However, no color was observed when the crystals of **2b** were exposed to UV radiation in a similar manner. Prolonged irradiation for 24 h in the Rayonet reactor at ca. 25 °C led to the formation of its benzocyclobutenol **7**, as monitored from TLC and ^{1}H NMR analyses.

For isolation of the cyclobutenol from solid state photolysis of **2b**, ca. 40-50 mg of the aldehyde crystals were photolyzed in a Rayonet reactor (λ = 350 nm) under nitrogen gas atmosphere. After 24h of irradiation, the initial crystallinity was found to be lost. The irradiated mixture was subjected silica gel column chromatography (10% ethyl acetate-hexanes) to isolate the cyclobutenol as a colorless solid.

For solution phase photolysis, the benzene solution of aldehyde **2b** (0.1 M) in a pyrex tube fitted with a septum was thoroughly purged with nitrogen gas for 15-20 min to remove the dissolved air. The solution was subsequently subjected to photolysis in the Rayonet reactor for 12 h. The solvent was removed from the photolysate *in vacuo* at room temperature and the residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR.

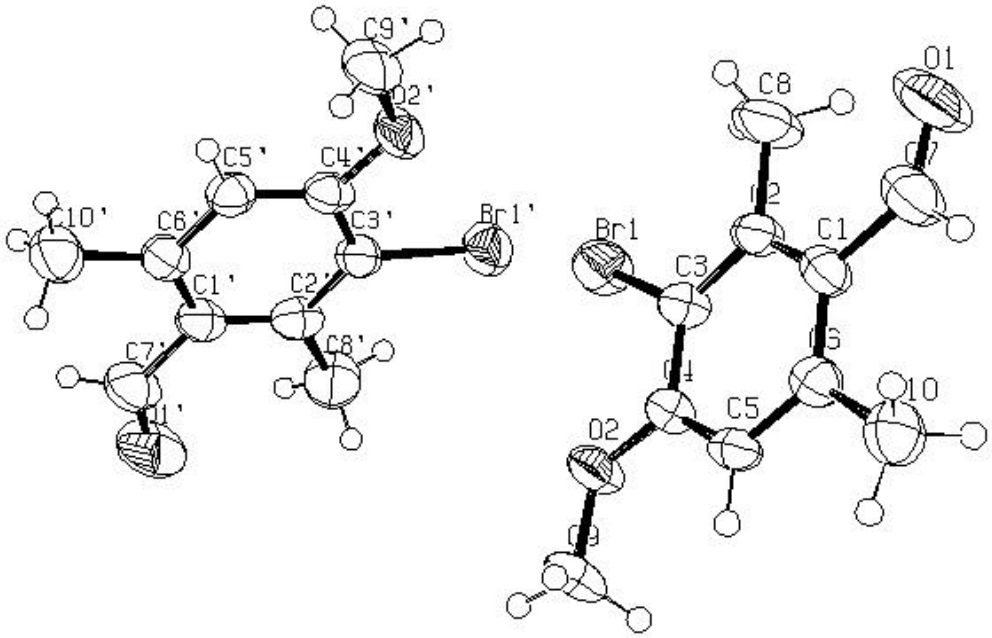

Figure S1. ORTEP drawing of the molecular structures of **2b** (two molecules in the asymmetric unit cell).

Table 1. Crystal data and structure refinement for 2,6-dimethyl-3-bromo-*p*-anisaldehyde (2b).

Identification code	**2b**	
Empirical formula	$C_{10}\ H_{11}\ Br\ O_2$	
Formula weight	243.10	
Temperature	293(2) K	
Diffractometer used	Siemens P4	
Radiation used, Wavelength	MoKa, 0.71073 Å	
Crystal system, Space group	Triclinic, P $\bar{1}$	
Unit cell dimensions	a = 8.112(1) Å	α= 82.89(1)°.
	b = 8.133(1) Å	β= 82.02(1)°.
	c = 15.195(2) Å	γ = 80.75(1)°.
Volume	974.6(2) $Å^3$	
Z, Calculated Density	4, 1.657 Mg/m^3	
Absorption coefficient	4.181 mm^{-1}	
F(000)	488	
Crystal size	0.29 x 0.22 x 0.18 mm	
Theta range for data collection	2.56 to 23.99°.	
Scan type	2θ-θ	
Scan speed	Variable, 2.0° to 60.0°/min. in ω	
Scan range (ω)	1.02° plus Kα separation	
Background measurement beginning	Stationary crystal and stationary counter at the	
	and end of scan, each for 25.0% of total scan time	
Index ranges	0≤h≤9, -8≤k≤9, -16≤l≤17	
Reflections collected	2784	
Independent reflections	2784	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2784 / 0 / 241	
Goodness-of-fit on F^2	1.039	
Weighting scheme	$1/[\sigma^2 (Fo^2)+(0.0485P)^2 +0.28P]$,	
$P=(\max(F_o^2,0)+2*F_c^2)/3$		
Data to parameter ratio	11.5:1	
Final R indices, 2236 reflections [I>2s(I)]	R1 = 0.0334, wR2 = 0.0806	
R indices (all data)	R1 = 0.0484, wR2 = 0.0878	
Largest diff. peak and hole	0.370 and -0.399 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2,6-dimethyl-3-bromo-*p*-anisaldehyde (2b). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2574(1)	-762(1)	3491(1)	59(1)
O(1)	1709(4)	-4807(5)	6813(2)	89(1)
O(2)	6134(3)	-891(3)	3642(2)	50(1)
C(1)	3867(4)	-3526(4)	5865(2)	42(1)
C(2)	2931(4)	-2769(5)	5165(3)	42(1)
C(3)	3738(4)	-1883(5)	4444(2)	41(1)
C(4)	5455(4)	-1749(4)	4390(2)	38(1)
C(5)	6333(4)	-2483(5)	5080(2)	39(1)
C(6)	5571(4)	-3360(5)	5829(2)	41(1)
C(7)	3104(6)	-4501(6)	6657(3)	61(1)
C(8)	1091(5)	-2898(7)	5192(3)	69(1)
C(9)	7900(4)	-829(5)	3550(3)	54(1)
C(10)	6620(5)	-4085(6)	6569(3)	58(1)
Br(1')	550(1)	2447(1)	1713(1)	60(1)
O(1')	4749(5)	3300(5)	-1584(3)	87(1)
O(2')	761(3)	-1103(3)	1547(2)	54(1)
C(1')	3331(4)	1176(5)	-694(2)	45(1)
C(2')	2535(4)	2113(5)	7(3)	46(1)
C(3')	1677(4)	1291(5)	737(2)	43(1)
C(4')	1600(4)	-427(5)	793(2)	42(1)
C(5')	2374(4)	-1305(5)	91(2)	43(1)
C(6')	3233(4)	-534(5)	-658(2)	45(1)
C(7')	4325(6)	1952(6)	-1488(3)	62(1)
C(8')	2579(6)	3981(6)	-25(3)	71(1)
C(9')	763(6)	-2872(5)	1645(3)	62(1)
C(10')	4048(5)	-1617(6)	-1394(3)	63(1)

Table 3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2,6-dimethyl-3-bromo-*p*-anisaldehyde (2b). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	43(1)	78(1)	55(1)	7(1)	-13(1)	-7(1)
O(1)	70(2)	111(3)	80(2)	15(2)	20(2)	-42(2)
O(2)	37(1)	64(2)	45(2)	10(1)	2(1)	-15(1)
C(1)	43(2)	41(2)	39(2)	-2(2)	5(2)	-11(2)
C(2)	31(2)	48(2)	50(2)	-11(2)	4(2)	-13(2)
C(3)	34(2)	42(2)	45(2)	-1(2)	-4(2)	-8(2)
C(4)	33(2)	40(2)	39(2)	-1(2)	0(1)	-9(1)
C(5)	28(2)	47(2)	44(2)	-3(2)	-2(1)	-12(2)
C(6)	41(2)	42(2)	40(2)	-2(2)	-4(2)	-9(2)
C(7)	58(3)	66(3)	55(3)	4(2)	8(2)	-22(2)
C(8)	36(2)	95(4)	75(3)	7(3)	-1(2)	-26(2)
C(9)	37(2)	62(3)	57(3)	6(2)	11(2)	-15(2)
C(10)	58(2)	69(3)	48(2)	3(2)	-8(2)	-12(2)
Br(1')	68(1)	55(1)	58(1)	-11(1)	4(1)	-12(1)
O(1')	92(2)	83(3)	80(3)	24(2)	6(2)	-38(2)
O(2')	65(2)	49(2)	46(2)	1(1)	11(1)	-20(1)
C(1')	43(2)	55(2)	38(2)	9(2)	-10(2)	-16(2)
C(2')	46(2)	44(2)	49(2)	9(2)	-13(2)	-12(2)
C(3')	41(2)	47(2)	42(2)	-3(2)	-6(2)	-10(2)
C(4')	41(2)	43(2)	42(2)	6(2)	-7(2)	-14(2)
C(5')	46(2)	40(2)	44(2)	-1(2)	-6(2)	-13(2)
C(6')	39(2)	56(2)	39(2)	1(2)	-8(2)	-9(2)
C(7')	62(3)	76(3)	49(3)	11(2)	-2(2)	-25(2)
C(8')	96(4)	49(3)	67(3)	2(2)	0(2)	-26(2)
C(9')	77(3)	46(3)	60(3)	8(2)	10(2)	-23(2)
C(10')	62(3)	75(3)	49(3)	-3(2)	-2(2)	-13(2)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2,6-dimethyl-3-bromo-*p*-anisaldehyde (2b).

	x	y	z	U(eq)
H(5A)	7469	-2392	5046	47
H(7A)	3809	-4930	7090	73
H(8A)	572	-1982	4815	103
H(8B)	552	-2859	5794	103
H(8C)	978	-3937	4983	103
H(9A)	8145	-232	4012	81
H(9B)	8241	-266	2976	81
H(9C)	8499	-1948	3601	81
H(10A)	7767	-3912	6388	88
H(10B)	6570	-5263	6692	88
H(10C)	6193	-3541	7097	88
H(5'A)	2317	-2444	121	52
H(7'A)	4653	1307	-1964	75
H(8'A)	1596	4488	327	106
H(8'B)	2598	4479	-632	106
H(8'C)	3568	4156	210	106
H(9'A)	149	-3160	1204	93
H(9'B)	239	-3213	2231	93
H(9'C)	1901	-3432	1566	93
H(10D)	3802	-2739	-1235	94
H(10E)	5244	-1626	-1467	94
H(10F)	3612	-1168	-1944	94