Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Photochemical Properties of Multi-Azobenzene Compounds – Electronic Supplementary Information –

Julia Bahrenburg, Claudia M. Sievers, Jan Boyke Schönborn, Bernd Hartke, Falk Renth, and Friedrich Temps

Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, D-24098 Kiel, Germany

Christian Näther

Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 6-7, D-24098 Kiel, Germany

Frank D. Sönnichsen

Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, D-24098 Kiel, Germany

Contents

1. Syntheses

All commercially available compounds were purchased from Merck, Sigma-Aldrich, Deutero and Lancaster and used without further purification, except for 4-aminoazobenze which was recrystallised from ethanol. Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (0.06-0.20 mm, Roth). All reactions were carried out under an argon atmosphere. NMR spectra were aquired with Bruker AC-200 and Bruker AV-600 spectrometers. MALDI mass spectra were recorded with a Biflex III instrument (Bruker) with 2,5-dihydroxybenzoic acid as matrix (0.5 mg in 1 ml toluene), CI mass spectra were recorded on a MAT 8200 (Finnigan). UV/VIS absorption spectra were taken on a Shimadzu UV-2401 desktop spectrometer.

1.1. 4-Iodoazobenzene (IAB)

3.40 mg (15.2 mmol) 4-iodoaniline were added to a solution of 2.01 g (18.2 mmol) nitrosobenzene in 130 ml glacial acetic acid. The mixture was stirred for 96 h at room temperature. Afterwards the mixture was diluted with 500 ml H_2O and extracted five times with 100 ml CH_2Cl_2 each. The organic layer was washed with brine (2 × 500 ml), dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The product (3.42 g, 11.1 mmol, 72 %) was purified by column chromatography. $R_f = 0.11$ (hexane/ethyl acetate, 200:1). ^{1}H NMR (200 MHz, 300 K, $CDCl_3$): $\delta = 7.89$ (d, 2H), 7.85 (d, 2H), 7.65 (d, 2H), 7.50 (m, 3H) ppm.

1.2. Bis[4-(phenylazo)phenyl]amine (BPAPA)

To a solution of 4 ml toluene were added one after the other under stirring 171 mg (0.850 mmol) AAB, 262 mg (0.850 mmol) IAB, 7.7 mg (0.038 mmol) 1,10-phenanthroline, 9.0 mg (0.047 mmol) copper(I)-iodide and 300 mg (2.54 mmol) potassium *tert*-butanolate. The mixture was heated to reflux at 130 °C within 30 min. After 5 h, the mixture was diluted and washed with 500 ml saturated aqueous $NaHCO_3$ solution, 500 ml diluted HCl and 500 ml H_2O and dried with Na_2SO_4. Evaporation of the solvent yielded the crude orange product which was purified by column chromatography ($R_f = 0.14$, toluene/hexane 2:1) and recrystallisation from a hexane-chloroform mixture (4:1). The reaction yielded 157 mg (416 mmol, 49 %) of the crystalline solid. ^{1}H NMR (600 MHz, 300 K, CD_3CN): $\delta =$ 7.92 (d, $J = 8.82$ Hz, 4H, 3-H), 7.88 (d, $J = 7.27$ Hz, 4H, 6-H), 7.64 (s, 1H, NH), 7.56 (t, J = 7.57, 7.57 Hz, 4H, 7-H), 7.50 (t, $J = 7.30$, 7.30 Hz, 2H, 8-H), 7.36 (d, $J = 8.84$ Hz, 4H, 2-H) ppm. ^{13}C NMR (150 MHz, 300 K, $CDCl_3$): $\delta = 152.9$ (C-5), 147.6 (C-1), 144.6 (C-4),

130.4 (C-8), 129.1 (C-7), 124.9 (C-3), 122.6 (C-6), 117.8 (C-2) ppm. MS (CI): $m/z = 377$. Anal. Calcd. for $C_{24}H_{19}N_5$: C, 76.37; H, 5.07; N, 18.56. Found: C, 76.63; H, 5.61; N, 17.81.

1.3. Tris[4-(phenylazo)phenyl]amine (TPAPA)

173 mg (0.860 mmol) AAB, 800 mg (2.60 mmol) IAB, 6.1 mg (0.030 mmol) 1,10-phenanthroline, 9.0 mg (0.047 mmol) copper(I)-iodide and 305 mg (2.58 mmol) potassium *tert*-butanolate were dissolved in 3 ml toluene. The mixture was heated to reflux at 130 °C for 5 h. Afterwards the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (50 ml) and washed with 500 ml water and 500 ml of diluted HCl solution. After drying with Na_2SO_4 and filtration, the solvent was removed in vacuo. The product was purified by column chromatography($R_f = 0.31$, toluene/hexane 2:1) and recrystallisation from a hexane-toluene mixture (5:1). The compound (177 mg, 317 mmol, 37 %) was obtained as red crystals. ^{1}H NMR (600 MHz, 300 K, $CDCl_3$): $\delta = 7.91$ (d, 6H, 3-H), 7.91 (d, 6H, 6-H), 7.52 (t, $J = 7.54$, 7.54 Hz, 6H, 7-H), 7.47 (t, $J = 7.28$, 7.28 Hz, 3H, 8-H), 7.32 (d, $J = 8.82$ Hz, 6H, 2-H), 7.36 (d, $J = 8.84$ Hz, 4H, 2-H) ppm. ^{13}C NMR (150 MHz, 300 K, $CDCl_3$): $\delta = 152.8$ (C-5), 149.0 (C-1 or C-4), 148.9 (C-4 or C-1), 130.8 (C-8), 129.1 (C-7), 124.7 (C-2), 124.5 (C-3), 122.8 (C-6) ppm. MS (MALDI): $m/z = 558$. Elementary analysis: See Ref. S1.

2. Table of calculated excited states

Table S1: Dominant excitations contributing to the lowest $n\pi^*$ and $\pi\pi^*$ excited electronic states of AAB, BPAPA and TPAPA.

compound	state	excitation		contribution	oscillator strength	excitation energy
		from	to	%		eV
AAB [a)]	$S_1(n\pi^*)$	HOMO−4	LUMO	90	4×10^{-5}	2.87
	$S_2(\pi\pi^*)$	HOMO	LUMO	91	8×10^{-1}	3.80
BPAPA	$S_1(n\pi^*)$	HOMO−8	LUMO	52	3×10^{-3}	2.82
		HOMO−9	LUMO+1	39		
	$S_2(n\pi^*)$	HOMO−9	LUMO	52	2×10^{-5}	2.82
		HOMO−8	LUMO+1	39		
	$S_3(\pi\pi^*)$	HOMO	LUMO	86	2×10^{0}	3.05
	$S_4(\pi\pi^*)$	HOMO	LUMO+1	83	9×10^{-2}	3.63
TPAPA	$S_1(n\pi^*)$	HOMO−14	LUMO+1	35	1×10^{-3}	2.81
		HOMO−14	LUMO	32		
		HOMO−14	LUMO+2	21		
	$S_2(n\pi^*)$	HOMO−13	LUMO	60	1×10^{-4}	2.81
		HOMO−13	LUMO+2	24		
	$S_3(n\pi^*)$	HOMO−12	LUMO+1	58	2×10^{-4}	2.81
		HOMO−12	LUMO+2	26		
	$S_4(\pi\pi^*)$	HOMO	LUMO	56	1×10^{0}	3.07
		HOMO	LUMO+1	28		
	$S_5(\pi\pi^*)$	HOMO	LUMO+1	57	1×10^{0}	3.08
		HOMO	LUMO	27		
	$S_6(\pi\pi^*)$	HOMO	LUMO+2	83	2×10^{-3}	3.74

[a)] Excited states for AAB at optimised OM2-MRCISD ground state structure with (8, 8) active space (Ref. S2).

3. NMR measurements

3.1. ^{1}H NMR spectra of TPAPA

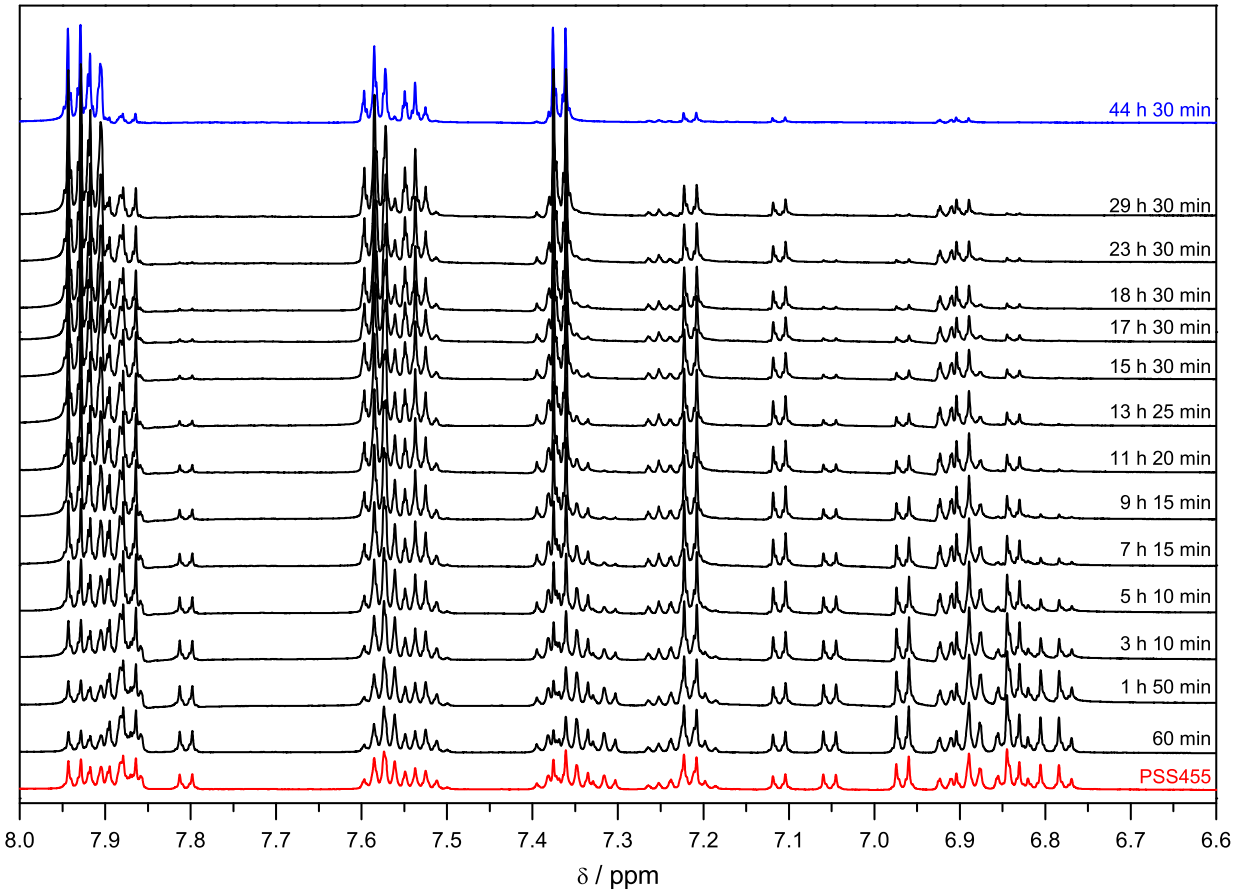

Fig. S1: ^{1}H NMR spectra of TPAPA in CD_3CN at $T = 35\,^\circ$C as function of time after excitation to the photostationary state PSS455 at $t = 0$.

3.2. 2D-HSQC NMR spectra of TPAPA

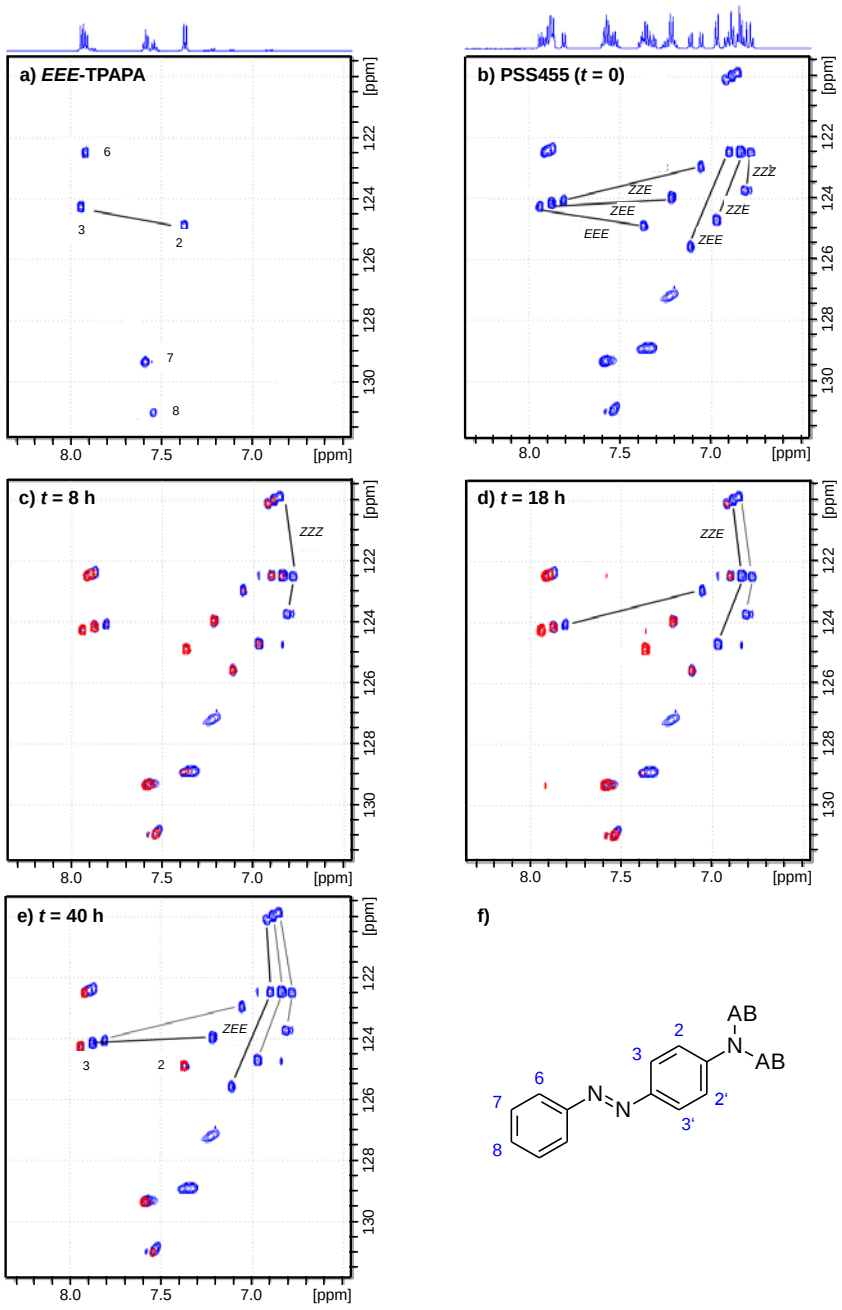

Fig. S2: 2D-HSQC NMR spectra of TPAPA in CD_3CN at $T = 35\,^{\circ}C$ at different times. a) Spectrum of the pure all-*E* isomer. b) Spectrum of TPAPA in the photostationary state PSS455 ($t = 0$). c) - e) Spectra after $t = 8$, 18, and 40 h (red), respectively, together with the spectra in the PSS455 (blue) from panel a) for reference. f) Assignments to the five chemically different proton sites for the all-*E* isomer identified by the labels 2, 3, and 6 – 8.

The 2D-HSQC spectra for the all-*E* isomer, for the photostationary state (PSS455), and for three selected times after preparation of the PSS show the coupling of the ^{13}C signals on the ordinate with the ^{1}H resonances of the H atoms bound the C atoms on the abscissa. The assignments for the *EEE*-isomer (Fig. S2a) to the five chemically different sites (labeled 2, 3, 6, 7, 8 in Fig. S2f) could be secured by means of COSY spectra. The key to the assignments for the other isomers was the observed change in the spectrum of the pure *EEE*-isomer in Fig. S2a to the spectrum of the photostationary state PSS455 in Fig. S2b. As can be seen, peaks 6, 7, and 8 show little change in spectral position, because they are associated with the outer aromatic rings that are too far away from the neighboring AB units to respond to their photoisomerisation. In contrast, resonances 2 and 3, which belong to the aromatic rings next to the central amino-N atom, split into several families of cross-peaks arising from the *ZEE*-, *ZZE*-, and *ZZZ*-isomers. The larger number of cross-peaks is due to the fact that the 2,2'- and 3,3'-positions (cf. Fig. S2f) are chemically equivalent only in the *EEE*-isomer, but distinguishable in the mixed photoisomers.

Since the thermal back-isomerisation from the PSS occurs sequentially, the additional cross-peaks could be assigned according to their observed time dependences (Figs. S2c–d). For example, in the spectrum in Fig. S2c shown in red at $t = 8$ h after preparation of the PSS, which has been superimposed on the spectrum of the PSS given in blue, the cross-peaks belonging to the *ZZZ*-isomer have virtually decayed to zero and are thereby identified by their blue color. Likewise, the cross-peaks belonging to the *ZZE*-isomer are reduced to nearly zero after $t = 18$ h (Fig. S2d). After $t = 40$ h, (Fig. S2d), the cross-peaks belonging to the *ZEE*-isomer eventually disappear as well such that only the *EEE*-isomer is left.

References

S1. T. Takahashi, T. Tanino, H. Ando, H. Nakano and Y. Shirota, Surface relief grating formation using a novel azobenzene-based photochromic amorphous molecular material, tris[4-(phenylazo)phenyl]amine. *Mol. Cryst. Liq. Cryst.*, 2005, **430**, 9–14.

S2. W. Thiel, MNDO program, version 6.1. Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany, 2007.