Supporting Information

Cis-Trans Isomerisation of Azobenzenes Studied by Laser-Coupled NMR Spectroscopy and DFT Calculations

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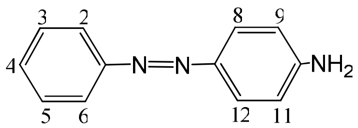
NMR spectra of AAB

AAB has six sets of protons that are magnetically and chemically non-equivalent, labelled **a-f** for the *trans* form and **g-l** for the *cis* form, as illustrated in Figure S1 (a) and (b). Positions 2/6 *ortho* to the azo bond are equivalent giving a doublet signal of intensity two and protons at positions 3/5, which are equivalent giving a triplet of intensity two. A proton at position 4 gives a triplet of intensity one. Positions 8/12 *ortho* to azo bond are equivalent and protons 9/11 are equivalent both giving a doublet signal of intensity two. Protons of the amino group give a singlet signal of intensity two. The 500 MHz one-dimensional (1D) ^{1}H NMR spectra associated with AAB at a concentration of 1.38 mM are shown in Figure S1. Prior to irradiation, as shown in Figure S1 (a) the NMR spectrum consists of six sets of signals corresponding to the six sets of protons in the *trans* form. All signals in Figure (a) were integrated to two protons which are equivalent, with the exception of the triplet signal **c** which were integrated to one proton equivalent, which was assigned to proton at position 4. The three doublet signals were assigned according to the shielding effect of the NH_2 group at position 10, protons at position 9/11 will resonate at the lowest frequency corresponding to signal **b**, followed by protons at position 8/12 corresponding to the signal **e**, followed by protons at position 2/6 corresponding to signal **f**. The second triplet signal **d** was assigned to protons at position 3/5. Finally, the singlet signal **a** was assigned to the protons of the amino group, its singlet nature indicating that the group is able to rotate freely on the NMR time-scale. The lack of any other significant signals in the 1D ^{1}H NMR spectrum of AAB indicated that in the dark the molecule existed in only one isomeric form that was assigned to the *trans* configuration based on abundance.



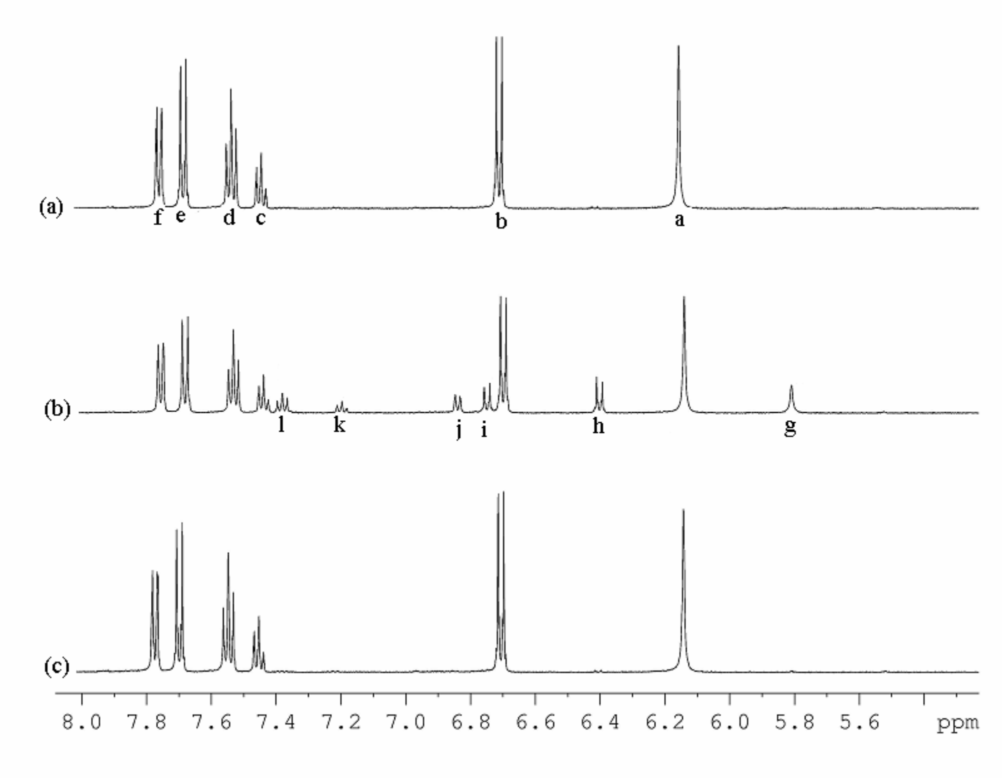


Figure S1 500 MHz 1D ^{1}H NMR spectra of AAB (1.38 mM) in d$_6$-DMSO (a) prior to irradiation, (b) at the 514 nm PSS, (c) after exposure of the PSS to darkness. TMS is the internal standard.

Irradiation of a 1.38 mM solution of AAB at 514 nm resulted in the appearance of a new set of signals as shown S1 (b), which provides clear evidence of a photoinduced event. The disappearance of these new signals in darkness and restoration of the starting spectrum, Figure (c), shows that the photoinduced event was thermally fully reversible, with no photodecomposition. These observations were interpreted as the occurrence of *trans-cis* isomerisation. According to the results obtained from the disperse dyes studied previously two pieces of information emerged; [7,8]

1. *Cis* isomer protons are consistently more shielded than their *trans* isomer counterparts.
2. Protons at position *ortho* to the azo linkage of the *trans* and *cis* isomers will resonate at significantly different positions, average $\Delta\delta$ ($=\delta_{cis}$-δ_{trans}) = −1.24 and −1.07 ppm in benzene and cyclohexane, respectively.

The new set of signals labelled **g-l** in Figure S1 (b) consists of six signals and was assigned due to the *cis* isomer as follows; the two doublet signals **j** and **i** were close match the doublet signals corresponding to protons at positions 2/6 and 8/12 of the *trans* isomer, respectively, resulting in a change in a chemical shift of -0.94 ppm and of -0.93 ppm for protons 2/6 and protons 8/12, respectively, values that are similar in magnitude to the previous recorded average values. The doublet signal **h** was assigned to protons at position 9/11. The two triplets **l** and **k** were close matches to the triplets signals corresponding to the protons at positions 3/5 and 4 of the *trans* isomer. Thus signal **l** was assigned to protons 3/5 and signal at **k** was assigned to the proton at position 4. Finally, the singlet signal **g** was assigned to protons of the NH_2 group. A summary of the *trans* and *cis* proton resonance assignments of AAB and the corresponding Δδ values is provided in Table Error! **No text of specified style in document.**S1.

Trans signal	*Cis* signal	Proton assignment	Δδ / ppm
a	g	NH_2	-0.33
b	h	9/11	-0.30
c	k	4	-0.24
d	l	3/5	-0.15
e	i	8/12	-0.94
f	j	2/6	-0.93

Table Error! No text of specified style in document.**S1 ^{1}H NMR assignments for the *trans* and *cis* isomers of AAB in d_6-DMSO, and the difference in chemical shift between *cis* and *trans* isomers, Δδ. largest values of Δδ are highlighted.**