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Synthesis and Photochemical Properties of Oligo-*ortho*-azobenzenes

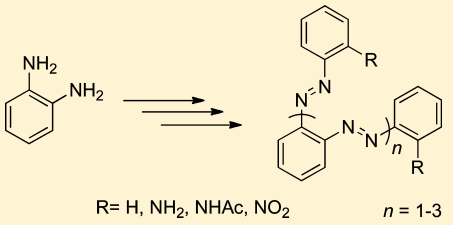
Silvia Bellotto,[†,‡] Raphael Reuter,[†] Christian Heinis,[‡] and Hermann A. Wegner*[,†]

[†]Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland

[‡]Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Supporting Information

ABSTRACT: Azobenzenes have attracted great interest in recent years because of their ability to change conformation upon irradiation. This property has been featured in several applications not only in organic chemistry but also in biology. Even though monoazobenzenes have been extensively studied and documented in the literature, only a few methods are available for the synthesis of oligo-*ortho*-azobenzenes. Also, their photochemical properties have not been reported so far. This study shows an efficient strategy for the preparation of oligo-*ortho*-azobenzenes and the investigation of their photochemical properties. It is demonstrated that the absorption spectra are highly influenced by the substituents. Interestingly, none of the *ortho*-bis-, tris-, or tetra-azobenzenes showed any $E \rightarrow Z$ isomerization. Only the *ortho*-nitrogen-substituted monoazobenzenes' photochromic behavior upon UV irradiation was observed.



INTRODUCTION

Since their discovery in the 19th century, azocompounds have been extensively used as dyes and pigments.[1] Therefore, several synthetic strategies have been developed to prepare azobenzene derivatives. Among all, the most relevant and common methods found in literature are the oxidation of anilines, the reduction of nitro-substituted aromatic compounds, the Mills reaction[2] (condensation of an aniline with a nitroso compound), and the diazo-coupling via diazonium salts.[3] Recently, a new synthetic strategy was proposed, in which a Pd-catalyzed coupling reaction was employed.[4] In addition to their use as colorants, a well-known property of azobenzenes is the photoisomerization from the *E* to the *Z* isomer and back.[5] The two isomers can be switched with ultraviolet light. The more intense absorption at 320 nm corresponds to the $\pi-\pi^*$ (S_2 state) transition, and irradiation at this wavelength leads to $E \rightarrow Z$ isomerization, whereas the *Z* isomer absorbs at longer wavelengths, around 430 nm, which is due to the $n-\pi^*$ (S_1 state) transition inducing $Z \rightarrow E$ isomerization. Since the *E* isomer is more stable by approximately 50 kJ/mol, the *Z* isomer can also easily relax back via $Z \rightarrow E$ isomerization upon heating.[6] Upon UV irradiation, the distance between the para carbon atoms decreases from about 9.0 Å in the *E* isomer to 5.5 Å in the *Z* form.[7] Thanks to this property, azo compounds have been employed for different uses and applications, such as in light controlled polymers,[8] liquid crystals,[9] surfaces,[10] and catalysts,[11] and were more recently found to be promising in controlling the structural and functional changes in biomolecules. Azobenzene derivatives, indeed, have been used for the photoswitching of proteins, like ion channels and receptors, and for the photocontrol of peptides,[12] nucleic acids, lipids, and carbohydrates.[13]

Compounds containing isolated azobenzenes have been already thoroughly investigated;[14−16] the interplay of multiple azobenzenes, however, has only been scarcely addressed. Bléger et al. investigated the photochromic and thermochromic behavior of four different *para*-bis(azo) connected by biphenyls.[17] Furthermore, the photochemical properties of a *meta*- and a *para*-bis(azo) derivative have been studied and compared. It has been shown that while the (*E*,*E*)-*m*-bisazobenzene has a similar behavior to the (*E*)-azobenzene, the (*E*,*E*)-*p*-azobenzene presents a red shift in the absorption spectrum and a lower photoreactivity upon UV irradiation.[18] The corresponding *ortho*-bis-azobenzenes, though, have not been investigated so far. One explanation might be the difficulties in the preparation of these structural themes with the known methods, making their synthesis quite challenging. Only a few examples have been reported in the literature. At the end of the 19th century, Mendola published a diazotization by sodium nitrite.[19] The synthesis of *ortho*-bis-azobenzenes, performed by Mills reaction in acetic acid and sodium acetate, was reported by Ruggli et al.[20−22] More recently, in addition to the preparations previously published by our group,[5] the treatment of azoxybenzenes with sodium sulphide[23] or a diazotization with sodium nitrite[24] have also been described for their synthesis. Herein, we present an efficient strategy for the preparation of oligo-*ortho*-azobenzenes and show the influence of conjugated azobenzene units and substituents in the ortho position on the photochemical properties.

RESULTS AND DISCUSSION

Even though several procedures are known for the synthesis of azobenzenes, none of them proved to be suitable for the preparation of *ortho*-nitrogen-substitued azobenzenes. The oxidative

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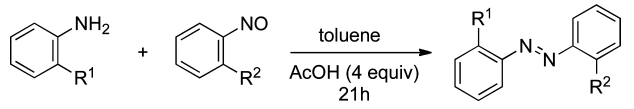
coupling with manganese dioxide, potassium superoxide, the reductive coupling with zinc and sodium hydroxide, a Pd-catalyzed strategy, and the Mills reaction were evaluated; none of them gave the expected product. For this reason, a method previously developed in our group was used,[5] in which the Mills reaction was modified using toluene as solvent and AcOH in stoichiometric amounts. Several *ortho*-nitrogen-substituted azobenzenes have been synthesized using these optimized conditions (Table 1).

Table 1. Synthesis of 2,2′-Dinitrogen-Substituted Azobenzenes 3



1 **2a: R= NHAc** **2b: R= H** **2c: R= NO_2** **3**

entry	R^1	R^2	T/°C	product (yield %)
1	NH_2	NHAc	60	**3a** (70)
2	NH_2	H	60	**3b** (33)
3	NH_2	NO_2	rt	**3c** (4)
4	H	NO_2	60	**3d** (24)
5	NO_2	H	60	**3e** (n.r.)
6	NO_2	NO_2	60	**3f** (n.r.)
7	NHAc	NHAc	60	**3g** (4)
8	NHAc	NO_2	60	**3h** (48)
9	NHAc	H	60	**3i** (11)
10	H	NHAc	60	**3i** (72)

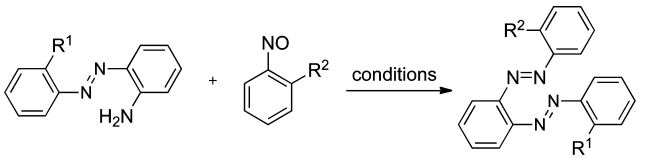
The efficiency of the reactions was shown to be dependent on the substituents. The reaction of entry 3 (Table 1) proceeded at rt because of the electron-withdrawing effect of the nitro group making the nitroso coupling partner **2** more reactive. However, 2-nitroaniline did not react either with nitrosobenzene (**2b**) (Table 1, entry 5) or 2-nitronitrosobenzene (**2c**) (Table 1, entry 6). Because of the presence of the nitro group in ortho position, the nucleophilicity of the amino group is greatly reduced toward an attack at the nitroso compound.

In order to obtain *ortho*-bis-azobenzenes, 2-amino-substituted azobenzenes **3a**, **3b**, and **3l** were subjected to the optimized Mills condition (AcOH, toluene). Interestingly, the classical condition (AcOH as solvent) gave, in most cases, superior results.

The reactivity of the nitroso compounds **2a**, **2b**, and **2c** was similar to the one observed for the 2-substitued-anilines influenced by the electron-withdrawing or -donating effect of the substituents. Indeed, thanks to the presence of the nitro group, the reaction of the diamine with 2-nitronitrosobenzene (**2c**) (Table 2, entry 3) was completed after a few minutes at rt under classical Mills conditions, whereas the other products were only obtained after longer reaction times at 60 °C. For example, when 2-nitrosoacetanilide (**2a**) was used, the reaction was completed after 2.5 days and the product was obtained in low yield (Table 2, entry 1). The reaction of entry 7 (Table 2) gave 2-phenylbenzotriazole as the main product. Only when 4 equiv of nitrosobenzene (**2b**) was used, the desired compound was obtained as the major product (Table 2, entry 7, condition C).

The different reactivity of *o*-phenylenediamine (**1a**) and 2-amino-substituted azobenzenes opens the possibility to obtain 2,2″-dinitrogen-substituted bisazobenzenes in a one-pot procedure.

Table 2. Synthesis of 2,2″-Dinitrogen-Substituted Bisazobenzenes 4



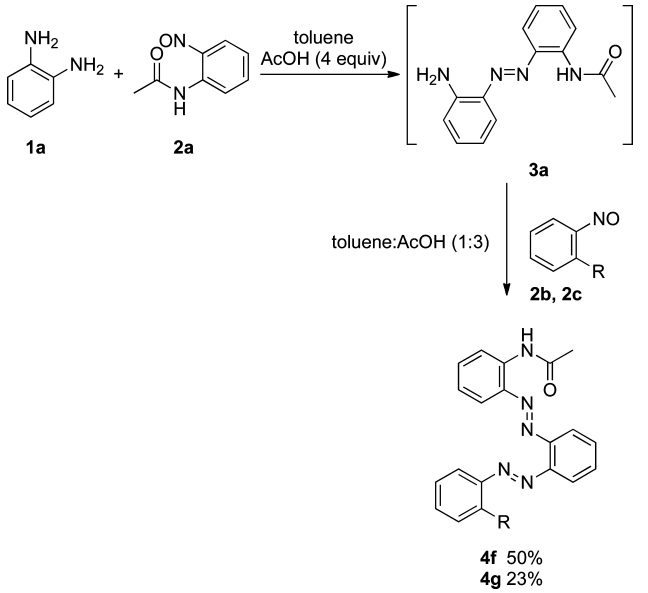
3 a-b-l **2 a-c** **4**

entry	R^1	R^2	T/°C	time	condition[a]	product (yield %)
1	NH_2	NHAc	60	2.5 d	B	**4a** (16)
2	NH_2	H	60	21 h	B	**4b** (16)
3	NH_2	NO_2	rt	15 min	A	**4c** (81)
4	H	NO_2	60	21 h	A	**4d** (17)
5	NHAc	NHAc	60	21 h	A	**4e** (44)
6	NHAc	NO_2	60	21 h	A	**4f** (66)
7	NHAc	H	60	21 h	A	**4g** (2)
					C	**4g** (44)

[a](A) AcOH; (B) toluene, AcOH (4 equiv); (C) **2** (4 equiv), toluene, AcOH (4 equiv).

The method was shown to be efficient for the preparation of the nonsymmetric 2,2″-disubstituted bis-*ortho*-azobenzenes. Indeed, compounds **4f** and **4g** were obtained in good to moderate yields starting from *o*-phenylenediamine (**1a**) (Scheme 1).

Scheme 1. One-Pot Preparation of Nonsymmetric 2,2″-Disubstituted Bis-*ortho*-azobenzenes



The same procedure was followed in the preparation of the symmetric 2,2″-disubstituted bis-*ortho*-azobenzenes (Scheme 2). When nitrosobenzene (**2b**) and *o*-phenylenediamine (**1a**) were subjected to the modified Mills conditions, the product **4h** was isolated after 3 days in 33% yield. However, the reaction with the 2-nitronitrosobenzene did not give the desired product.

Unfortunately, the same protocol was not applicable for the synthesis of symmetric 2,2‴-disubstituted tris-*ortho*-azobenzenes **5** (Scheme 3).

Therefore, a stepwise approach was chosen to access 2,2‴-disubstituted tris-*ortho*-azobenzenes with different substituents

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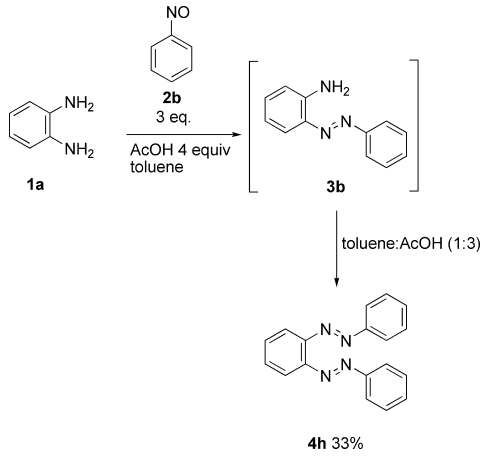
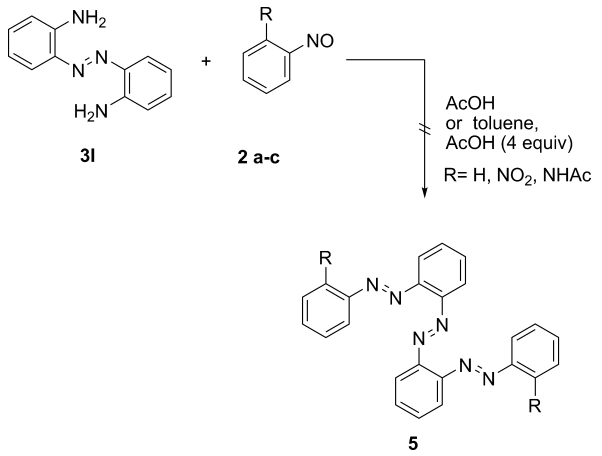
Scheme 2. One-Pot Preparation of the Symmetric 2,2″-Disubstituted Bis-*ortho*-azobenzene 4h



Scheme 3. Attempted One-Pot Preparation of Symmetric 2,2″-Disubstituted Tris-*ortho*-azobenzenes 5



(Scheme 4). The modified Mills reaction was found to be the best procedure. It was observed that the higher the number of the azobonds, the longer the reaction time. Indeed, the reaction required 8 days to provide the product in acceptable yield. The synthesis of the 2,2‴″-disubstituted tetra-*ortho*-azobenzenes was performed only for the dinitro-*ortho*-substituted **6**. As expected from the reactivity previously observed, the reaction was finished after only 4 days. The product was obtained in a moderate yield (25%) compared to the tris-*ortho*-azobenzenes **5a** and **5b**.

Other nonsymmetric 2,2″-disubstituted tris-*ortho*-azobenzenes were synthesized according to the strategy shown in Scheme 5 relying on the one-pot procedure to prepare the key intermediate **3a**. The deprotection of compound **4g** gave the amino-substituted bisazobenzene **4b**, followed by Mills reaction. The coupling with 2-nitrosoacetanilide (**2a**) and nitrosobenzene (**2b**) did not provide any of the desired product. When 2-nitronitrosobenzene (**2c**) was used, the reaction occurred and the corresponding tris-*ortho*-azobenzene **5c** was obtained after 6 days in 21% yield. Again, this reactivity can be rationalized by the reduced electron density of the nitroso functionality due to the electron-withdrawing effect of the nitro group.

Accordingly, a similar strategy gave 2-nitro-2‴-acetamido-tris-*ortho*-azobenzene (**5f**) as presented in Scheme 6. The ortho-substituted diamine **3l** was obtained by deprotection of 2-acetamido-2′-aminoazobenzene (**3a**). The following two Mills reactions gave first compound **4a** in 59% and the final product **5f** in 58% yield, respectively.

With all the different oligo-*ortho*-azobenzenes in hand, the photochemical properties were studied. The absorption spectra were acquired, and the photoisomerization behavior was assessed. In particular, the influence of the conjugated systems and of the substituents was investigated. First, the absorption spectra of the *ortho*-nitrogen-substituted monoazobenzenes were measured in chloroform. All of them showed the typical $\pi-\pi^*$ transition at around 320 nm. However, depending on the substituents, specific characteristics can be distinguished. In all the amino substituted azobenzenes, where a free NH_2 group is present, the spectra present a broad peak at around 450 nm. The presence of the nitro group causes a slight bathochromic shift of the spectrum. This shift is also observed when the second substituent is an acetamido group or a free amino group. In the case where the nitro group is the only substituent, the spectrum is highly similar to the one of the azobenzene (Figure 1a). If all the acetamido substituted azobenzenes are compared, the presence of shoulders at around 400 nm is observed (see the Supporting Information).

All the *ortho*-nitrogen substituted monoazobenzenes were irradiated at 365 nm, and the switching ability was analyzed by UV-spectroscopy[25] (Figure 1b–d; see the Supporting Information for details). Compound **3i** followed the classical well-known behavior of azobenzene (Figure 1d). Indeed, the absorbance increased at 450 nm and decreased at 320 nm until it reached the photostationary state after a few seconds of irradiation. It completely relaxed back after 2 h at rt. Compounds **3a**, **3b** (Figure 1b), **3c**, **3d** (Figure 1c), **3g**, **3h**, and **3l**, after exposure to UV light, showed a decrease in absorbance for all transitions (see the Supporting Information for details). The photoisomerization was reversible even after several cycles of irradiation for all the monoazobenzenes. Furthermore, all compounds except **3d** (Figure 1c) showed a higher absorbance than the initial state after incubation at rt, especially if kept in the dark (**3c**, **3g**, **3h**, **3l**, see the Supporting Information), and could be completely converted back after exposure to visible light indicating a mixture of *E* and *Z* isomers in the photostationary state at these conditions. It was also shown that the presence of electron-withdrawing groups caused only small changes in the absorbance (compound **3d**, Figure 1c, for compounds **3c** and **3h**, see the Supporting Information). Bandara et al. have also demonstrated the influence of substituents on the photoswitching behavior of azobenzene compounds. They describe that in their system, based on azo-(aminomethyl)-pyridine compounds, the presence of electron-donating groups reduces the photoisomerization properties. Similar to what we observed, they reported a decreased absorbance for both transitions upon UV irradiation.[26] This behavior is unusual, since the *Z* isomer of azobenzene normally shows an increased intensity for the $n-\pi^*$ transition. Consequently a photochemical $E \rightarrow Z$ isomerization is observed after irradiation with visible light, whereas for most azobenzenes a $Z \rightarrow E$ isomerization takes place if irradiated at 450 nm.

The absorption spectra of the bis-*ortho*-azobenzenes showed a similar behavior as for the monoazobenzenes (Figure 2). Indeed, as previously described, the nitro group caused a small shift in the spectra, whereas the presence of the amino group was easily detectable because of the broad and high absorbance at around 450 nm. Once again, the acetamido-substituted compounds showed the typical pattern with three maxima at 340, 400, and 470 nm. Furthermore, close to the $\pi-\pi^*$

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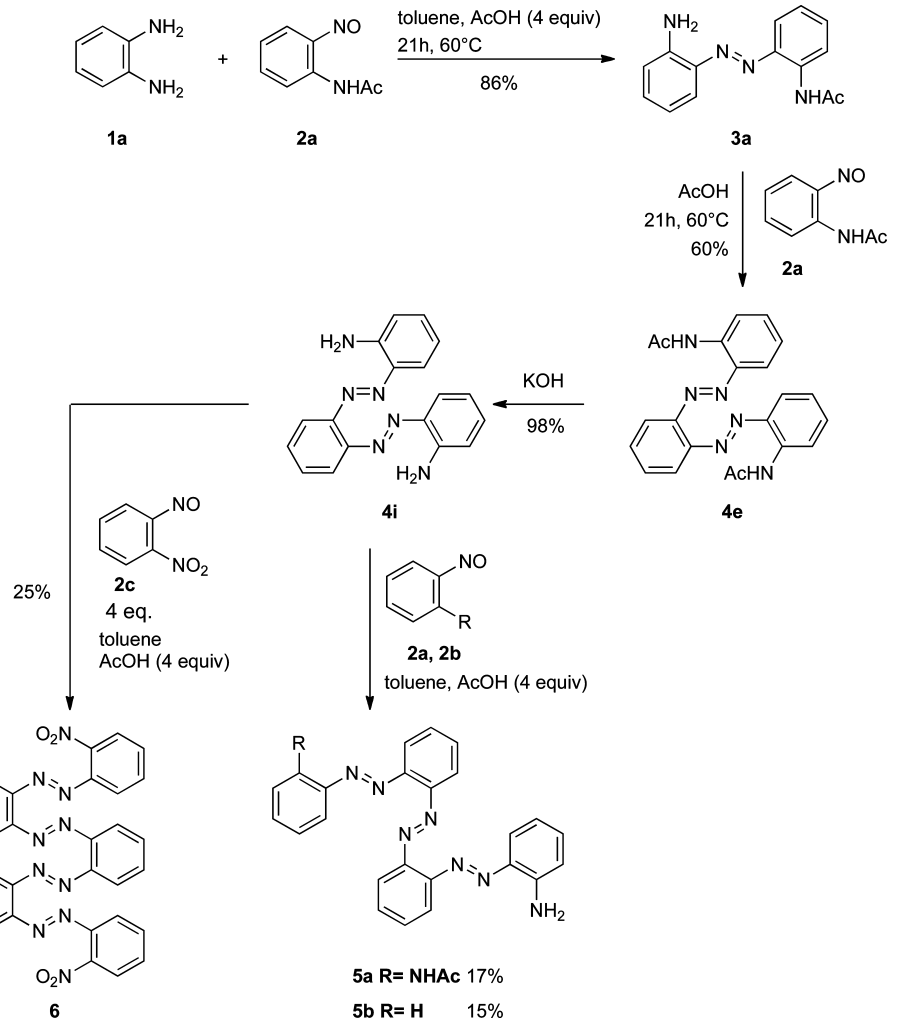
Scheme 4. Synthesis of Nonsymmetric 2,2‴-Disubstitued Tris-*ortho*-azobenzenes



transition at around 350 nm, an additional shoulder can be noticed, which is present in all bis-*ortho*-azobenzenes. In the case of the diamino-substituted derivative **4i** and 2-nitro-2‴acetamido-bisazobenzene (**4f**) (see the Supporting Information), only a broadening of the absorption can be seen.

In contrast to the switching behavior observed for mono-azobenzenes, none of bis-*ortho*-azobenzenes switched upon UV irradiation. Cisnetti and co-workers have demonstrated that (*E*,*E*)-*m*-bisazobenzene behaves similarly to azobenzene and that (*E*,*E*)-*p*-bisazobenzene also isomerizes although a decreased photoreactivity, has been observed.[18] The authors explain this fact by the larger electronic coupling in the *p*-bisazobenzene compared to the *m*-bisazobenzene, which they confirmed by quantum chemical calculations. If this increased electronic communication is the reason for the reduced isomerization, *o*-bisazobenzenes should exhibit an even lower isomerization tendency. Indeed, in our case, all the tested compounds showed complete inertness toward photoisomerization. One possible alternative explanation would be that the back-isomerization is faster than the minimum time required for the measurement (5 s). Flash photolysis studies have not been done so far to rule out this option.

An analogous behavior was also observed for the tri- and tetra-azobenzenes (Figure 3). The amino group causes also in these cases an increased absorbance at around 450 nm. The additional absorption caused by the acetamido group is less evident. The spectrum of tetra-azobenzene **6** is comparable to the one of **4d** and **5c** because of the presence of the nitro groups. None of these compounds show isomerization upon UV irradiation as it was previously observed for the bis-*ortho*-azobenzenes.

■ CONCLUSIONS

A stepwise convenient strategy for the preparation of oligo-*ortho*-azobenzenes and a one-pot procedure for the synthesis of bis-*ortho*-azobenzenes have been presented. The photochemical properties of these compounds have been thoroughly investigated. It has been shown that the absorption spectra exhibit common features depending on the substituent. Additionally, only the *ortho*-nitrogen-substituted monoazobenzenes isomerized upon UV irradiation. Furthermore, the presence of electron-withdrawing groups induced a decreased photochromism. Current efforts in the group address the reason for the inhibition of the photochromism by substitution with another azobenzene moiety in the ortho position.

■ EXPERIMENTAL SECTION

2-Nitrosoacetanilide (2a). A solution of *o*-phenylenediamine (**1a**) (10.0 g, 92.5 mmol, 1.00 equiv) in 150 mL of EtOAc was cooled down below 5 °C. Then, an ice-cold solution of acetic anhydride (9.12 mL, 97.1 mmol, 1.05 equiv) in 80 mL of EtOAc was added, and the

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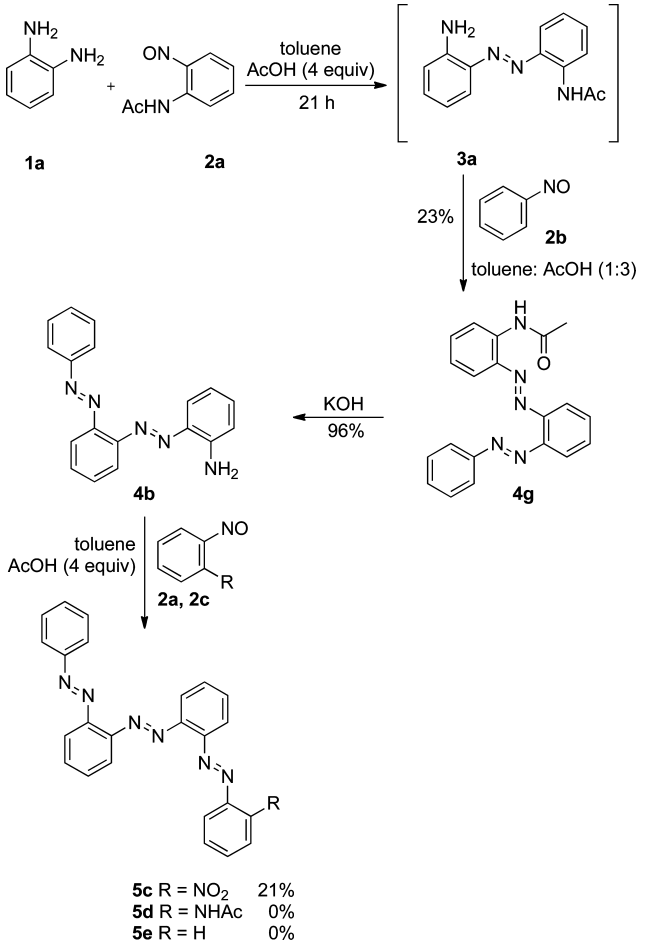
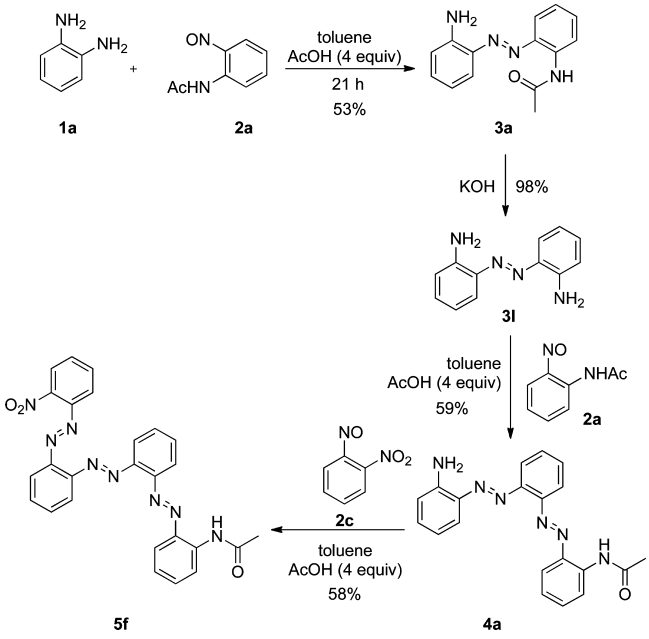
Scheme 5. Synthesis of Nonsymmetric 2,2‴-Disubstitued Tris-*ortho*-azobenzenes



Scheme 6. Synthesis of 2-Nitro-2‴-acetamido-tris-*ortho*-azobenzenes (5f)



mixture was stirred for 20 min. The precipitate that was obtained was filtered with a glass filter under vacuum to give 5.13 g (37%) of 2-aminoacetanilide: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.15 (dd, J = 7.8, 1.2 Hz, 1H), 6.92−6.85 (m, 1H), 6.70 (dd, J = 8.0, 1.3 Hz, 1H), 6.53 (td, J = 7.6, 1.4 Hz, 1H), 4.84 (s, 2H), 2.03 (s, 3H). The analytical data correspond to the literature.[27] The acetylated diamine (5.00 g, 33.3 mmol, 1.00 equiv) was suspended in 50 mL of CH_2Cl_2. Oxone (30.7 g, 49.9 mmol, 1.50 equiv), dissolved in 200 mL of water, was added and stirred fiercely for 1 h at rt. The organic phase was separated, and the aqueous phase was extracted with 100 mL of CH_2Cl_2. The combined organic phases were washed with 1 m HCl (100 mL), saturated aq $NaHCO_3$ (100 mL), and water (100 mL). It was then dried over $MgSO_4$, concentrated, and purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and the product was obtained as green solid (2.41 g, 44% yield): mp 107−108 °C (lit. mp 106−107 °C);[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.85 (dd, J = 8.6, 1.0 Hz, 1H), 7.71 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.32 (s, 1H), 7.22−7.08 (m, 1H), 2.35 (s, 3H). The analytical data correspond to the literature.[5]

2-Nitronitrosobenzene (2c). Oxone (20.0 g, 32.6 mmol, 1.50 equiv) was treated with 24 mL of concentrated H_2SO_4. The suspension was then poured onto 130 g of crushed ice, and the mixture was stirred at rt until all of the ice had melted. Then, 2-nitroaniline (3.00 g, 21.7 mmol, 1.00 equiv) was added and stirred at rt for 20 h. The mixture was extracted twice with 150 mL of CH_2Cl_2 and dried over $MgSO_4$, the solvent was removed, and the title compound was obtained as a brown solid (3.12 g, 94%): mp 119−122 °C (lit. 135−137 °C);[29] ^{1}H NMR (400 MHz $CDCl_3$) δ 8.17 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H). The compound **2c** is in equilibrium with its dimer, and the analytical data correspond to the literature.[30]

General Procedure for the Mills Reaction Using AcOH (Condition A). A solution of amine (1.00 equiv) in acetic acid (7 mL/mmol) was degassed with a nitrogen stream for 15 min. Then, the nitroso compound **2** (1.00 equiv) was added. The mixture was stirred at 60 °C for 21 h, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

General Procedure for the Mills Reaction Using AcOH/Toluene (Condition B). A solution of amine (1.00 equiv) in toluene (7 mL/mmol) was degassed with a nitrogen stream for 15 min. Then, the nitroso compound (1.00 equiv) and acetic acid (4.00 equiv) were added. The mixture was stirred at 60 °C for 21 h, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

General Procedure for the Mills Reaction Using AcOH/Toluene (Condition C). A solution of amine (1.00 equiv) in toluene (7 mL/mmol) was degassed with a nitrogen stream for 15 min. Then, the nitroso compound (4.00 equiv) and acetic acid (4.00 equiv) were added. The mixture was stirred at 60 °C for 21 h, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

2-Acetamido-2′-amino-*ortho*-azobenzene (3a). The title compound **3a** was prepared according to general procedures (condition B) from *o*-phenylenediamine (**1a**) (0.821 g, 7.58 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (1.25 g, 7.71 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 1:1), and the title compound was obtained as red solid in 70% yield (1.35 g): mp 148−150 °C (lit. 143 °C);[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.63 (d, J = 8.3 Hz, 1H), 7.70 (dd, J = 8.1, 1.6 Hz, 1H), 7.62 (dd, J = 8.1, 1.3 Hz, 1H), 7.45−7.37 (m, 1H), 7.29−7.22 (m, 1H), 7.18−7.10 (m, 1H), 6.87−6.71 (m, 2H), 5.40 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 145.0, 137.5, 135.5, 133.2, 131.8, 124.4, 123.5, 122.2, 120.5, 120.2, 118.0, 117.4, 25.5.

2-Amino-*ortho*-azobenzene (3b). The title compound **3b** was prepared according to general procedures (condition B) from *o*-phenylenediamine (**1a**) (0.820 g, 7.58 mmol, 1.00 equiv) and nitrosobenzene (**2b**) (812 mg, 7.58 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1), and the title compound was obtained as brown solid in 33% yield (498 mg): mp 58−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 3H),

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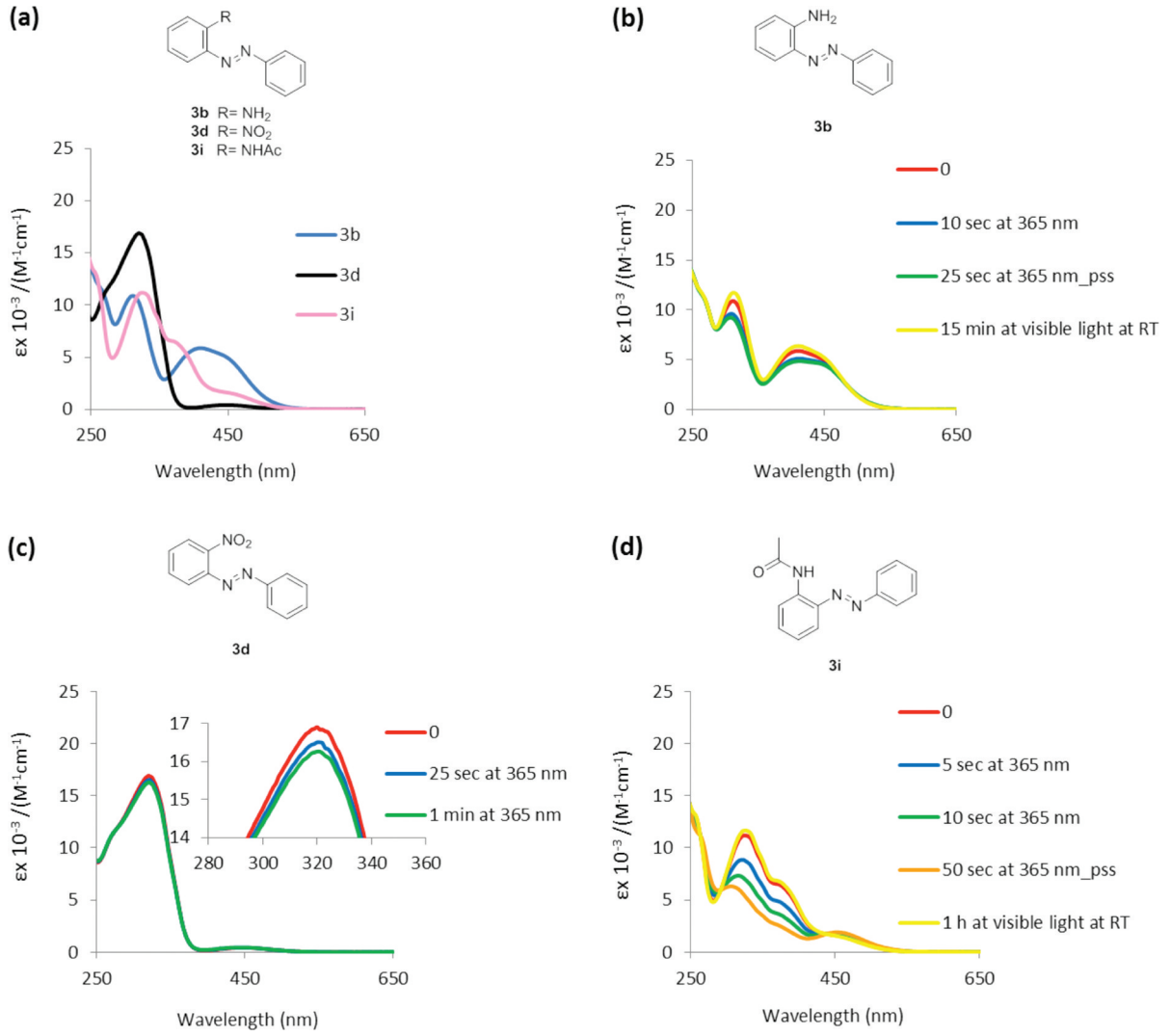

Figure 1. Absorption spectra (a) and photoisomerization of representative *ortho*-amino-, nitro-, and acetamido-substituted monoazobenzenes (**3b**, **3d**, and **3i**, respectively; b–d) in chloroform.

7.53–7.47 (m, 2H), 7.45–7.39 (m, 1H), 7.22 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 6.83 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 6.77 (dd, J = 8.2, 1.1 Hz, 1H), 5.90 (s, 2H). The analytical data correspond to the literature.[32]

2-Amino-2′-nitro-*ortho*-azobenzene (3c). The title compound **3c** was prepared according to general procedures (condition B) from *o*-phenylenediamine (**1a**) (0.820 g, 7.58 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (1.15 g, 7.58 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1) followed by preparative TLC (SiO_2, hexane/$CHCl_3$, 1:1), and the title compound was obtained as brown solid in 4% yield (73.2 mg): mp 95–97 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.05 (dd, J = 8.1, 1.2 Hz, 1H), 7.92 (dd, J = 8.1, 1.2 Hz, 1H), 7.84–7.76 (m, 1H), 7.68–7.60 (m, 2H), 7.36 (s, 2H), 7.26 (ddd, J = 8.4, 6.9, 1.6 Hz, 1H), 6.88 (dd, J = 8.4, 1.0 Hz, 1H), 6.69 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 146.7, 145.0, 144.2, 135.9, 134.1, 133.4, 130.0, 127.7, 124.1, 118.0, 117.4, 115.9; MS (EI, 70 eV) m/z (%) = 242 (57%) [M^+], 92 (100%); $C_{12}H_{10}N_4O_2$ (242.24) calcd C 59.50, H 4.16, N 23.13; found C 59.35, H 4.14, N 22.88.

2-Nitro-*ortho*-azobenzene (3d). The title compound **3d** was prepared according to general procedures (condition B) from aniline (0.827 mL, 9.07 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (1.38 g, 9.07 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 3:1), and the title compound was obtained as an orange-brown solid in 24% yield (502 mg): mp 66–70 °C (lit. 67–68 °C);[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.89 (m, 3H), 7.72–7.65 (m, 2H), 7.62–7.49 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 147.6, 145.6, 133.2, 132.4, 130.6, 129.4 (2C), 124.2, 123.8 (2C), 118.6.

2,2′-Diacetamido-*ortho*-azobenzene (3g). The title compound **3g** was prepared according to general procedures (condition B) from *N*-(2-aminophenyl)acetamide (495 mg, 3.30 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (541 mg, 3.30 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, DCM/EtOAc, 1:1), and 41.3 mg of orange product were obtained (4% yield): mp 273–275 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 2H), 8.68 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.7 Hz, 2H), 2.30 (s, 6H). The analytical data correspond to the literature.[34]

2-Acetamido-2′nitro-*ortho*-azobenzene (3h). The title compound **3h** was prepared according to general procedures (condition B) from *N*-(2-aminophenyl)acetamide (500 mg, 3.31 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (506 mg, 3.33 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 1:1). The solvent was evaporated and the orange product was obtained in 48% yield (449 mg): mp 143–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.74 (d, J = 8.5 Hz, 1H), 7.93 (dd, J = 8.0, 1.4 Hz, 2H), 7.81 (dd, J = 8.0, 1.5 Hz, 1H), 7.74 (td, J = 7.7, 1.4 Hz, 1H), 7.61 (ddd, J = 8.0, 7.4, 1.5 Hz, 1H), 7.57–7.47 (m, 1H), 7.22 (ddd, J = 8.6, 7.3, 1.3 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 146.2, 144.8, 138.9, 135.0, 134.6, 133.4, 130.9, 126.7,

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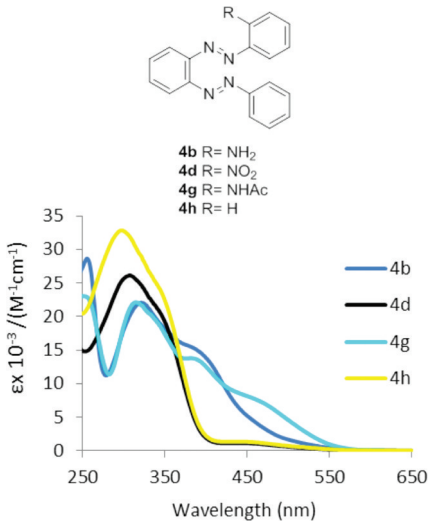

Figure 2. Absorption spectra of a representative *ortho*-amino-, nitro-, acetamido-, and hydrogen-substituted bis-azobenzenes (**4b**, **4d**, **4g**, and **4h**, respectively) in chloroform.

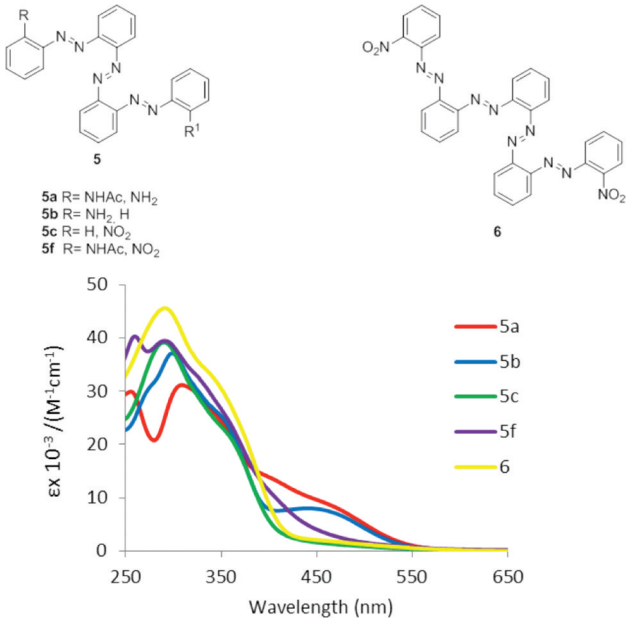

Figure 3. Absorption spectra of the disubstitued tris- and tetra-*ortho*-azobenzenes in chloroform.

124.5, 123.6, 120.9, 120.3, 25.4; MS (EI, 70 eV) *m*/*z* (%) = 284 (48%) [M^+], 134 (100%); $C_{14}H_{12}N_4O_3$ (284.27) calcd C 59.15, H 4.25, N 19.71; found C 59.09, H 4.25, N 19.85.

2-Acetamido-*ortho*-azobenzene (3i). The title compound **3i** was prepared according to general procedures (condition B) from aniline (0.294 mL, 3.22 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (529 mg, 3.22 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 1:1), and 555 mg of yellow product were obtained (72% yield). The same product was also prepared according to general procedures (condition B) from 2-acetamido-2′-amino-*ortho*-azobenzene (**3a**) (470 mg, 3.13 mmol, 1.00 equiv) and nitrosobenzene (**2b**) (357 mg, 3.33 mmol, 1.07 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and 80.1 mg of yellow product was obtained (11%): mp 124–127 °C (lit. 127–129 °C);[35] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.68 (d, J = 8.4 Hz, 1H), 7.91–7.81 (m, 3H), 7.58–7.50 (m, 3H), 7.50–7.45 (m, 1H), 7.21–7.14 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 152.5, 138.9, 136.1, 133.1, 132.0, 129.5 (2C), 123.5, 122.8 (2C), 121.3, 120.4, 25.5.

2,2′-Diamino-*ortho*-azobenzene (3l). A solution of *o*-phenylenediamine (**1a**) (0.764 g, 7.07 mmol, 1.00 equiv) in toluene (50 mL) was degassed with a nitrogen stream for 15 min. Then, 2-nitrosoacetamide (1.16 g, 7.07 mmol, 1.00 equiv) and acetic acid (1.62 mL) were added. The mixture was stirred at 60 °C for 21 h, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and the compound **3a** was obtained as red solid (0.792 g, 44% yield). Then, a solution of 2-acetamido-2′-amino-*ortho*-azobenzene (**3a**) (740 mg, 2.91 mmol, 1.00 equiv) in ethanol (138 mL) was treated with a solution of KOH (12.1 g, 215 mmol, 74.0 equiv) in ethanol (80 mL) and water (32 mL). The mixture was heated to 90 °C. After 1 h, the mixture was poured onto ice (500 g) and extracted with CH_2Cl_2 (3 × 100 mL). It was dried over Na_2SO_4 and concentrated to yield 0.583 g (94%): mp 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.0, 1.4 Hz, 2H), 7.21–7.14 (m, 2H), 6.83–6.74 (m, 4H), 5.49 (s, 4H). The analytical data correspond to the literature.[5]

2-Acetamido-2″-amino-*ortho*-bisazobenzene (4a). The title compound **4a** was prepared according to general procedures (condition B) from 2,2′-diaminodiazobenzene (**3l**) (300 mg, 1.41 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (230 mg, 1.41 mmol, 1.00 equiv). After 2.5 days, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1). The product was obtained as a red solid (80.3 mg, 16%): mp 158–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.69 (d, J = 8.3 Hz, 1H), 7.88 (dd, J = 8.1, 1.5 Hz, 1H), 7.85 (dd, J = 8.1, 1.5 Hz, 1H), 7.81 (dd, J = 7.9, 1.5 Hz, 1H), 7.72 (dd, J = 7.7, 1.6 Hz, 1H), 7.62–7.44 (m, 3H), 7.20 (ddd, J = 15.3, 8.4, 1.4 Hz, 2H), 6.87–6.81 (m, 1H), 6.74 (dd, J = 8.2, 1.0 Hz, 1H), 6.31 (s, 2H), 2.00 (s, 3H). The analytical data correspond to the literature.[5]

2-Amino-*ortho*-bisazobenzene (4b). The title compound **4b** was prepared according to general procedures (condition B) from 2,2′-diaminodiazobenzene (**3l**) (0.250 g, 1.19 mmol, 1.00 equiv) and nitrosobenzene (**2b**) (130 mg, 1.19 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1). The product was obtained as a brown solid (57.1 mg, 16%): mp 97–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.0, 1.6 Hz, 1H), 7.95–7.88 (m, 3H), 7.76 (dd, J = 8.0, 1.4 Hz, 1H), 7.62–7.45 (m, 5H), 7.21 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 6.86 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 6.74 (dd, J = 8.3, 1.1 Hz, 1H), 6.69 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 148.1, 147.9, 141.5, 138.0, 133.2, 132.3, 131.7, 131.4, 130.4, 129.3 (2C), 123.3 (2C), 117.3, 117.2, 117.1, 116.4; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{15}N_5^+$ [M + H^+] 302.1406, found 302.1400.

2-Amino-2″-nitro-*ortho*-bisazobenzene (4c). To a round-bottom flask was added the 2,2′-diaminoazobenzene (**3l**) (80.0 mg, 0.377 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (57.3 mg, 0.377 mmol, 1.00 equiv) followed by AcOH (11 mL). The mixture was stirred for 15 min. Then, water was added (50 mL/mmol), and the liquid was carefully turned basic with sodium carbonate (2 M Na_2CO_3 in H_2O, 5 mL/1 mL AcOH). The mixture was then extracted with CH_2Cl_2 (3 × 20 mL/mmol) and dried over $MgSO_4$, and the solvent was removed. The residual black solid was resuspended in CH_2Cl_2 and purified by flash column chromatography (SiO_2, DCM/hexane 1:1). The product was obtained as a brown solid (106 mg, 81%): mp 111–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.0 Hz, 2H), 7.91 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.72–7.67 (m, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.62–7.56 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 6.9 Hz, 1H), 6.87 (dd, J = 8.1, 7.0 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.62 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.7, 147.4, 146.2, 141.7, 138.0, 133.3, 133.1, 133.0, 132.6, 130.6, 130.4, 124.3, 119.0, 117.31, 117.30, 117.26, 117.0; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{15}N_6O_2^+$ [M + H^+] 347.1251, found 347.1260.

2-Nitro-*ortho*-bisazobenzene (4d). The title compound **4d** was prepared according to general procedures (condition A) from 2-amino-*ortho*-azobenzene (**3b**) (200 mg, 1.01 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (154 mg, 1.01 mmol, 1.00 equiv). The mixture was stirred for 21 h at 60 °C. The solvent was removed under

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reduced pressure, and HCl (1 M aq solvent; 25 mL) was added. The mixture was then extracted with CH_2Cl_2 (2 × 30 mL) and purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1). An oily orange solution was obtained (57.2 mg) in 17% yield: mp 61−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.97 (m, 2H), 7.97−7.93 (m, 1H), 7.83−7.78 (m, 1H), 7.76 (dd, J = 7.9, 1.4 Hz, 1H), 7.69 (dd, J = 5.2, 2.0 Hz, 2H), 7.67−7.61 (m, 1H), 7.61−7.50 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 149.2, 147.6 (2C), 146.0, 133.3, 132.5, 131.7, 131.2, 130.7, 129.3 (2C), 124.3, 123.5 (2C), 119.11, 119.09, 117.9; HRMS (ESI) m/z calcd for $C_{18}H_{14}N_5O_2^+$ [M + H$^+$] 332.1142, found 332.1148.

2,2″-Diacetamido-*ortho*-bisazobenzene (4e). The title compound **4e** was prepared according to general procedures (condition A) from 2-acetamido-2′-amino-*ortho*-azobenzene (**3a**) (187 mg, 0.735 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (123 mg, 0.749 mmol, 1.02 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 1:2), and 130 mg of product were obtained (44%): mp 182−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 2H), 8.69 (d, J = 8.3 Hz, 2H), 7.86 (dd, J = 8.1, 1.4 Hz, 2H), 7.76 (dd, J = 6.0, 3.4 Hz, 2H), 7.65 (dd, J = 6.0, 3.4 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.7 Hz, 2H), 1.91 (s, 6H). The analytical data correspond to the literature.[5]

2-Acetamido-2″-nitro-*ortho*-bisazobenzene (4f). The title compound **4f** was prepared according to general procedures (condition A) from 2-acetamido-2′-amino-*ortho*-azobenzene (**3a**) (0.101 g, 0.393 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (59.8 mg, 0.393 mmol, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and 103 mg of orange product were obtained (66%): mp 136−138 °C; ^{1}H NMR (400 MHz, DMSO) δ 10.19 (s, 1H), 8.32−8.27 (m, 1H), 8.15 (dd, J = 7.8, 1.5 Hz, 1H), 8.01 (dd, J = 8.0, 1.3 Hz, 1H), 7.88−7.71 (m, 5H), 7.66 (dd, J = 7.8, 1.5 Hz, 1H), 7.62 (dd, J = 8.0, 1.3 Hz, 1H), 7.59−7.53 (m, 1H), 7.27−7.20 (m, 1H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 148.8, 147.3, 147.1, 146.1, 139.4, 134.8, 133.6, 133.4, 132.8, 131.5, 130.1, 126.2, 124.4, 123.5, 120.6, 119.1, 118.8, 117.8, 25.2; MS (EI, 70 eV) m/z (%) = 388 (51%) [M$^+$], 106 (100%); $C_{20}H_{16}N_6O_3$ (388.39) calcd C 61.85, H 4.15, N 21.64; found C 61.46, H 4.17, N 21.50.

2-Acetamido-*ortho*-bisazobenzene (4g). The title compound **4g** was prepared according to general procedures (condition C) from 2-acetamido-2′-amino-*ortho*-azobenzene (**3a**) (195 mg, 0.767 mmol, 1.00 equiv) and nitrosobenzene (**2b**) (337 mg, 3.15 mmol, 4.00 equiv). After 3 h, the reaction was finished, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 1:1), and 116 mg (44%) of orange product were obtained: mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.70 (dd, J = 8.4, 1.1 Hz, 1H), 7.99 (dd, J = 8.1, 1.6 Hz, 1H), 7.92−7.87 (m, 2H), 7.85 (dd, J = 7.8, 1.6 Hz, 1H), 7.71 (dd, J = 7.7, 1.7 Hz, 1H), 7.61 (dqd, J = 14.8, 7.3, 1.6 Hz, 2H), 7.55−7.45 (m, 4H), 7.25−7.19 (m, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 153.0, 149.7, 148.1, 147.1, 139.4, 135.2, 133.3, 131.8, 131.2, 129.4 (2C), 125.1, 123.4, 123.3 (2C), 120.6, 120.2, 118.0, 25.0; MS (EI, 70 eV) m/z (%) = 343 (83%) [M$^+$], 106 (100%); $C_{20}H_{17}N_5O$ (343.39) calcd C 69.96, H 4.99, N 20.40; found C 69.84, H 4.96, N 20.42.

2,2″-Diamino-bis-*ortho*-azobenzene (4i). A solution of 2,2″-diacetamido-*ortho*-bisazobenzene (**4e**) (3.76 g, 9.39 mmol, 1.00 equiv) in ethanol (341 mL) was treated with a solution of KOH (30.4 g, 542 mmol, 57.7 equiv) in ethanol (200 mL) and water (77 mL). The mixture was heated to 90 °C. After 1.5 h, the mixture was poured onto ice (1.20 kg), extracted with CH_2Cl_2 (3 × 200 mL), dried over Na_2SO_4, and concentrated to yield a red oil (2.96 g), which crystallized in the refrigerator overnight (99%): mp 95−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.1, 1.5 Hz, 2H), 7.81−7.75 (m, 2H), 7.53−7.46 (m, 2H), 7.21 (ddd, J = 8.4, 7.1, 1.6 Hz, 2H), 6.87−6.81 (m, 2H), 6.75 (dt, J = 8.2, 3.9 Hz, 2H), 6.27 (s, 4H). The analytical data correspond to the literature.[5]

One-Pot Preparation of Symmetric 2,2″-Disubstituted Bis-*ortho*-azobenzenes (4h). A solution of *ortho*-phenylendiamine (**1a**) (200 mg, 1.85 mmol, 1.00 equiv) in toluene (36 mL) was degassed with a nitrogen stream for 15 min. Then, nitrosobenzene (**2b**) (594 mg, 5.55 mmol, 3.00 equiv) and AcOH (215 μL, 3.75 mmol, 2.00 equiv) were added. The mixture was stirred at 60 °C for 18 h, and more AcOH (108 mL) was added. After 2 days the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1), and the solid that was obtained was recrystallized from EtOH to obtain 177 mg of a brown solid (33%): mp 106−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 4H), 7.79−7.73 (m, 2H), 7.61−7.46 (m, 8H). The analytical data correspond to the literature.[23]

General Procedure for One-Pot Preparation of Nonsymmetric 2,2″-Disubstitued Bis-*ortho*-azobenzenes (Condition D). A solution of *o*-phenylendiamine (**1a**) (1.00 equiv) in toluene (7 mL/mmol) was degassed under a nitrogen stream for 15 min. Then, the first nitroso compound (1.10 equiv) and AcOH (4.00 equiv) were added. The mixture was stirred at 60 °C for 18 h, and the second nitroso compound (1.00 equiv) and more acetic acid (toluene/acetic acid, 1:3) were added. After 1 day the solvent was removed under reduced pressure. The residue was purified by flash column chromatography.

One-Pot Preparation of 2,2″-Disubstituted Bis-*ortho*-azobenzenes (4f). The title compound **4f** was prepared according to general procedures (condition D) from *o*-phenylenediamine (**1a**) (250 mg, 2.31 mmol, 1.00 equiv), 2-nitrosoacetanilide (**2a**) (417 mg, 2.54 mmol, 1.10 equiv), and 2-nitronitrosobenzene (**2c**) (352 mg, 2.31, 1.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and the product **4f** was obtained as an orange solid (450 mg, 50%).

One-Pot Preparation of 2,2″-Disubstituted Bis-*ortho*-azobenzenes (4g). The title compound **4g** was prepared according to general procedures (condition D) from *o*-phenylendiamine (**1a**) (1.80 g, 16.6 mmol, 1.00 equiv), 2-nitrosoacetanilide (**2a**) (2.73 g, 16.6 mmol, 1.00 equiv), and nitrosobenzene (**2b**) (7.13 g, 66.6, 4.00 equiv). The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and the product was obtained in 23% yield (1.32 g).

2-Amino-2‴-acetamido-tris-*ortho*-azobenzene (5a). The title compound **5a** was prepared according to general procedures (condition B) from 2,2″-diamino-bis-*ortho*-azobenzene (**4i**) (250 mg, 0.790 mmol, 1.00 equiv) and 2-nitrosoacetanilide (**2a**) (131 mg, 0.869 mmol, 1.10 equiv). After 8 d the solvent was evaporated, the reaction mixture was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1 to 1:3), and the product was obtained in 17% yield (73.1 mg): mp 177−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.68 (d, J = 8.4 Hz, 1H), 7.99 (dd, J = 8.0, 1.6 Hz, 1H), 7.91 (dd, J = 3.5, 1.4 Hz, 1H), 7.89 (dd, J = 3.5, 1.4 Hz, 1H), 7.88−7.85 (m, 1H), 7.72−7.57 (m, 5H), 7.51−7.42 (m, 2H), 7.24−7.19 (m, 1H), 7.19−7.13 (m, 1H), 6.84−6.78 (m, 1H), 6.67 (dd, J = 8.2, 1.0 Hz, 1H), 6.53 (s, 2H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 148.3, 148.1 (2C), 147.7, 141.71, 139.3, 137.9, 134.5, 133.3, 132.54, 132.50, 132.2, 131.6, 131.3, 130.2, 127.0, 123.4, 120.6, 119.5, 118.0, 117.8, 117.24, 117.22, 116.9, 25.2; HRMS (ESI) m/z calcd for $C_{26}H_{22}N_8O^+$ [M + H$^+$] 463.1989, found 463.1997.

2-Amino-tris-*ortho*-azobenzene 5b. The title compound **5b** was prepared according to general procedures (condition B) from 2,2″-diamine-bis-*ortho*-azobenzene (**4i**) (250 mg, 0.790 mmol, 1.00 equiv) and nitrosobenzene (**2b**) (84.6 mg, 0.790 mmol, 1.00 equiv). After 6 days the solvent was removed, the reaction mixture was purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1), and the product was obtained in 50% yield (128 mg): mp 156−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.0, 1.6 Hz, 3H), 7.92−7.88 (m, 1H), 7.82 (dd, J = 8.0, 1.3 Hz, 1H), 7.79−7.75 (m, 1H), 7.70 (dd, J = 7.3, 2.1 Hz, 1H), 7.64−7.54 (m, 3H), 7.54−7.43 (m, 4H), 7.22−7.15 (m, 1H), 6.84 (t, J = 7.0 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 6.64 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 148.7, 148.5 (2C), 148.0, 141.5, 137.9, 133.3, 132.3, 132.1, 131.5, 131.2, 131.0, 130.3, 129.3 (2C), 123.4 (2C), 118.61, 118.57, 117.4, 117.3, 117.0, 116.5; HRMS (ESI) m/z calcd for $C_{24}H_{19}N_7^+$ [M + H$^+$] 406,1775, found 406.1779.

2-Nitro-tris-*ortho*-azobenzene 5c. The title compound **5c** was prepared according to general procedures (condition B) from

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2-amino-*ortho*-bisazobenzene (**4b**) (300 mg, 0.996 mmol, 1.00 equiv) in toluene (10.0 mL) and 2-nitronitrosobenzene (**2c**) (167 mg, 1.10 mmol, 1.10 equiv) After 6 days the solvent was removed under reduced pressure, and the product was purified by flash column chromatography (SiO_2, hexane/EtOAc, 7:1 to 1:3) to give the product in 21% yield (91.1 mg): mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.81 (m, 5H), 7.80−7.70 (m, 2H), 7.69−7.55 (m, 5H), 7.54−7.38 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 149.1, 148.5, 148.4, 147.6, 145.7, 135.0, 133.2, 132.3, 131.7, 131.6, 131.5, 131.0, 130.6, 129.2 (2C), 124.0, 123.3 (2C), 120.0, 118.9, 118.7, 118.3, 117.9; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{17}N_7O_2^+$ [M + H$^+$] 436.1516, found 436.1522.

2-Acetamido-2‴-nitro-tris-*ortho*-azobenzene 5f. The title compound **5f** was prepared according to general procedures (condition B) from 2-acetamido-2″-amino-*ortho*-bisazobenzene (**4a**) (368 mg, 1.03 mmol, 1.00 equiv) in toluene (17 mL) and 2-nitronitrosobenzene (**2c**) (172 mg, 1.13 mmol, 1.10 equiv). After 6 d the solvent was removed under reduced pressure, and the product was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1) to give the product in 58% yield (293 mg): mp 162−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.62 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.87−7.80 (m, 3H), 7.76 (ddd, *J* = 13.4, 7.9, 1.8 Hz, 2H), 7.70−7.57 (m, 4H), 7.55−7.44 (m, 3H), 7.44−7.38 (m, 1H), 7.20−7.13 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 149.2, 148.2, 147.7, 147.6, 147.0, 145.5, 139.2, 134.2, 133.3, 133.0, 132.3, 132.1, 131.6, 131.4, 130.8, 127.5, 124.1, 123.3, 120.6, 120.5, 118.7, 118.5, 118.4, 118.1, 25.0; MS (FAB) *m*/*z* (%) = 493 (81%) [M$^+$], 345 (100%); $C_{26}H_{20}N_8O_3$ (492.49) calcd C 63.41, H 4.09, N 22.75; found C 63.42, H 4.14, N 22.60.

2,2⁗-Dinitro-tetra-*ortho*-azobenzene 6. The title compound **6** was prepared according to general procedures (condition B) from diamine-bis-*ortho*-azobenzene (**4i**) (250 mg, 0.790 mmol, 1.00 equiv) and 2-nitronitrosobenzene (**2c**) (361 mg, 2.37 mmol, 3.00 equiv). After 4 days the solvent was removed, the reaction mixture was purified by flash column chromatography (SiO_2, hexane/EtOAc, 2:1), and the product was obtained in 25% yield (114 mg): mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.83 (m, 4H), 7.80−7.74 (m, 2H), 7.64 (tt, *J* = 5.0, 2.5 Hz, 4H), 7.59−7.46 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 148.4, 147.7 (2C), 145.6, 133.2, 132.3, 131.7, 131.6, 130.9, 124.0, 119.6, 119.0, 118.8, 117.8; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{20}N_{10}O_4^+$ [M + H$^+$] 585.1742, found 585.1752.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **3c**, **3h**, **4b**, **4c**, **4d**, **4f**, **4g**, **5a**, **5b**, **5c**, **5f**, **6**; absorption spectra of all *ortho*-amino, acetamido and nitro substituted monoazobenzenes and *ortho*-amino, acetamido, nitro and hydrogen substituted bis-azobenzenes; photoisomerization of compounds **3a**, **3c**, **3g**, **3h**, **3l**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hermann.wegner@unibas.ch.

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