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Photoswitchable Azoheterocycles via Coupling of Lithiated Imidazoles with Benzenediazonium Salts

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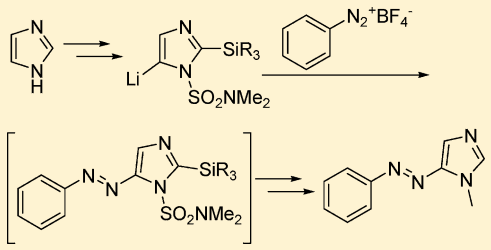
Supporting Information

ABSTRACT: In contrast to azobenzenes, heterocyclic azo compounds are less well investigated. Phenylazoimidazoles would be versatile as photodissociable ligands (PDLs) because imidazole is an important donor in coordination chemistry. Here, we present the synthesis of 4- and 5-phenylazoimidazoles via a novel azo-coupling method. 1,2-Protected imidazole is lithiated in the 5-position and coupled with benzenediazonium tetrafluoroborate. Several new phenylazoimidazoles were prepared. They exhibit an excellent switching behavior. Upon irradiation of the *trans* isomers with UV light, >95% of the *cis* forms are obtained. Upon heating, a complete transformation back to the *trans* configuration was achieved. Back switching with visible light, however, is incomplete.



INTRODUCTION

Azobenzenes are known to undergo photochemical *cis*/*trans*-isomerization and therefore have been extensively used as molecular switches to achieve a number of dynamic, machine-like functions.[1] While azobenzenes are well investigated,[2] the class of heterocyclic azo compounds has been largely neglected. Azopyridines have been used as photodissociable ligands (PDLs).[3−7] For instance, 3-azopyridines coordinate to Ni-porphyrins in their *trans* configuration forming paramagnetic complexes. Upon irradiation, the *trans*-azopyridines undergo isomerization to the *cis*-forms, which for sterical reasons dissociate forming the diamagnetic square planar Ni-porphyrins without axial ligands (light-driven coordination-induced spin state switch, LD-CISSS).[8−10] Phenylazoimidazoles would be an interesting class of photoswitchable ligands, particularly of PDLs because imidazoles are much stronger donor ligands as compared to pyridines leading to larger association constants with transition metals.[11]

There are three possible regioisomers of azoimidazoles with the azo group in the 2, 4, or 5 position (Figure1).

It is known that substitution of imidazoles in the 2 position severely hinders axial binding to metal porphyrins.[12] For instance, imidazole binds almost 3 orders of magnitude better to Fe(III)TPP chloride than 2-methylimidazole, whereas substitution at the 5 position has almost no effect.[13] For imidazoles that are substituted in the 4 position, a similar steric effect in lowering the binding constant can be expected as in 2-substituted imidazoles. To develop photodissociative ligands with strong axial binding to metal prophyrins we therefore set out to synthesize 5-azophenylimidazoles.

There are reports on several 2-substituted 4(5)-phenylazoimidazoles and 2-phenylazoimidazoles which are synthesized by azo coupling of imidazole with benzene diazonium salts.[14,15] However, unsubstituted 4(5)-phenylazoimidazoles (**1**), which are needed for the design of PDLs could not be synthesized on a large scale so far. Only traces were found in the composition of 2-phenylazoimidazole (**2**).[14,16] The condensation of 4(5)-aminoimidazole with nitrosobenzene (which is one of the standard methods to prepare azobenzenes) cannot be applied because 4(5)-aminoimidazole is not a stable compound.[17,18] For the synthesis of 4(5)-phenylazoimidazoles we therefore developed an alternative route.

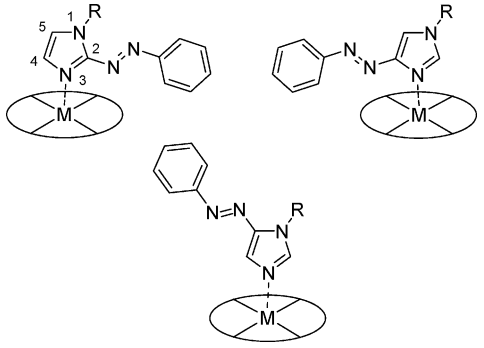


Figure 1. Regioisomers of N-substituted azoimidazoles and simplified binding modes as axial ligands to porphyrins.

We here report on a convenient synthesis of a number of 5-substituted imidazoles from 1-dimethylsulfamyolimidazole (**3**).[19] After the 2-position is blocked with a silyl group the selective activation of the 5-position can be performed with butyllithium.[20,21] Reaction with electrophiles, e.g., alkyl bromides, yields the corresponding 5-substituted imidazoles.[22] Our strategy to synthesize 5-azoimidazoles now is based on the reaction of the 5-lithiated imidazole with diazonium salts as the

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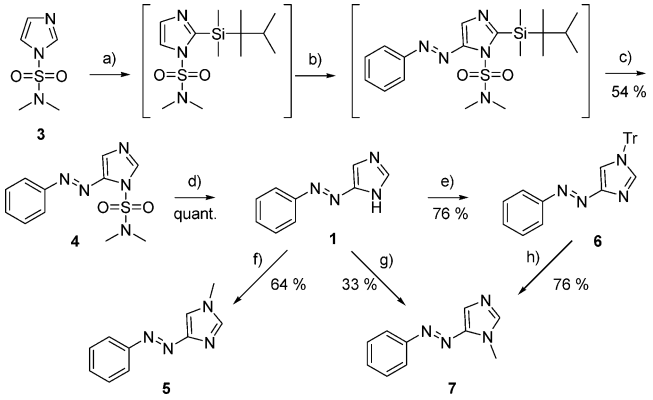
electrophile. To the best of our knowledge, azo compounds were never prepared via this route. So far, only phenyl Grignard compounds,[23−25] diphenylmercury,[26] and triphenylindium[27] have been used as the organometallic component in azo-coupling reactions.

RESULTS AND DISCUSSION

Synthesis. Although the 2-silyl-protected imidazoles are isolable it was found to be more convenient to lithiate at the 5-position in situ with a second equilibrium of butyllithium.[20] The 5-lithio derivate was converted to the phenylazoimidazole by reaction with diazonium benzenetetrafluoroborate (Scheme 1). Deprotection with tetrabutylammonium fluoride leads to 1-

Scheme 1. Synthesis of 4- and 5-Phenylazoimidazoles[a]



[a]Reagents and conditions: (a) *n*-BuLi, −78 °C, THF, 30 min, then DMTSCl, rt, 16 h; (b) *n*-BuLi, −78 °C, THF, 30 min, then $C_6H_5N_2^+BF_4^-$, rt, 16 h; (c) TBAF, THF, rt, 2 h; (d) EtOH/HCl 4:1, 80 °C, 3 h; (e) TrCl, acetonitrile, rt, 16 h; (f) NaH, THF, 0 °C to rt, 10 min, then MeI, 0 °C to rt, 3 h; (g) Me_2SO_4, 20% aq. KOH, rt, 2 h; (h) MeOTf, CH_2Cl_2, rt, 16 h, then acetone/water 1:1, rt, 3 h.

dimethylsulfamoyl-5-phenylazoimidazole (**4**) in 54% yield over three steps. A crystal structure determination confirmed the 5-position of the azo group (see the Supporting Information). Compound **4** exhibits the desired regiochemistry for coordination; however, dimethylsulfamoyl is a strong electron-withdrawing group, which weakens the donor strength of the imidazole. Therefore, the sulfamoyl group was quantitatively removed by treatment with acid, giving the 4(5)-phenylazoimidazole (**1**). To prevent tautomerism between the 4- and 5-phenylazoimidazole, the imidazole ring was N-methylated. Direct methylation can result in two products, which can be easily distinguished by HMBC. Methyl iodide leads only to the unwanted 1-methyl-4-phenylazoimidazole (**5**) (64% yield). Dimethyl sulfate as the methylating agent gives mainly 1-methyl-5-phenylazoimidazole (**7**), however, in poor yields (33%), and alongside with the regioisomer **5** (17%). Higher yields (58%) of pure **7** were obtained by a two pot, three step procedure. Introduction of a trityl group gives exclusively 1-trityl-4-phenylazoimidazole (**6**). Methylation with methyl triflate and removal of the trityl group leads to the desired phenylazoimidazole **7**.

To check the applicability of the phenylazoimidazoles as photodissociable ligands (PDLs), we investigated the switching behavior of **1** and **4**−**7**. UV spectra were measured, and the photostationary states were determined at 297, 365, 440, and 455 nm. The thermal back isomerization (*cis* to *trans* form) was monitored by ^{1}H NMR.

As expected, irradiation of *trans*-4(5)-phenylazoimidazole (**1**) did not lead to a detectable concentration of the *cis* configuration at room temperature. A similar behavior was observed for 2-phenylazoimidazole (**2**).[15] Sinha et al. demonstrated that the *cis* form of **2** is indeed formed by irradiation; however, its lifetime is very short. The *cis* configuration isomerizes back to the *trans* form by a proton-assisted mechanism via a hydrazone intermediate (for proposed mechanisms, see the Supporting Information). We suggest an analogous mechanism for 4(5)-phenylazoimidazole (**1**). This is corroborated by low-temperature NMR measurements. Upon irradiation at −78 °C we observed new signals in the ^{1}H NMR spectrum that are assigned to the *cis*-form of 4(5)-phenylazoimidazole (**1**) and that disappear upon warming the solution.

As opposed to **1**, the N-substituted phenylazoimidazoles are stable in their *cis* form[28] for 5−500 h at room temperature (Table 1). Conversion from *trans* to *cis* is achieved upon

Table 1. Conversion of the Phenylazoimidazoles 4−7 to the *Cis* Forms[a]

azoimidazole	maximum *cis* (%)	half lives (h)
4	95	39.7
5	95	4.7
6	96	320
7	98	528

[a]The photostationary states are obtained upon irradiation with UV light of 365 nm, and the half lives of the *cis* forms were measured at 25 °C by ^{1}H NMR.

irradiation with UV light of 365 nm. The photostationary states contain between 95 and 98% of the *cis* isomer. Both were determined by ^{1}H NMR spectroscopy.

Thus, the switching efficiency for *trans*−*cis* isomerization of **7** (98% cis isomer) is superior to parent azobenzene (91%)[29] and azopyridine (91%).[6] With a half-life of more than 500 h, *cis*-5-phenylazoimidazole **7** is more stable than the *cis* configurations of most azobenzenes and azopyridines.

According to ^{1}H NMR spectra and DFT calculations, the *cis* configurations of the phenylazoimidazoles **4**−**7** exhibit unusual conformations. In the *trans* configuration of azoimidazole **7** the proton at C4 resonates at 7.60 ppm in chloroform-d_1 which is in the expected range (compare 7.14 ppm in the parent imidazole); however, in the *cis* form the corresponding signal appears at 5.44 ppm. Similar upfield shifts were detected in the *cis* isomers of the azoimidazoles **4**−**6** (see the Supporting Information). DFT calculations (at the B3LYP/6-31G* level of theory) revealed the reason for these anomalous shifts. In contrast to the *cis* isomer of azobenzene where both phenyl rings are twisted out of planarity by about 56° with respect to the C−N═N−C plane,[30] the imidazole ring in *cis*-**7** is coplanar and the phenyl ring is perfectly orthogonal (90°) with respect with the C−N═N−C plane (Figure 2, top), which prevents conjugation between the two rings. The proton at C4 of the imidazole ring protudes into the deshielding range of the phenyl ring, which gives rise to the upfield shift. The *trans* configurations of **4**−**7** exhibit the expected planar geometries. The difference in conjugation in the *cis* and *trans* isomer of **7** is well represented by ACID calculations.[31,32] The ACID plot (Figure 2, bottom) reveals a contiguous isosurface of the

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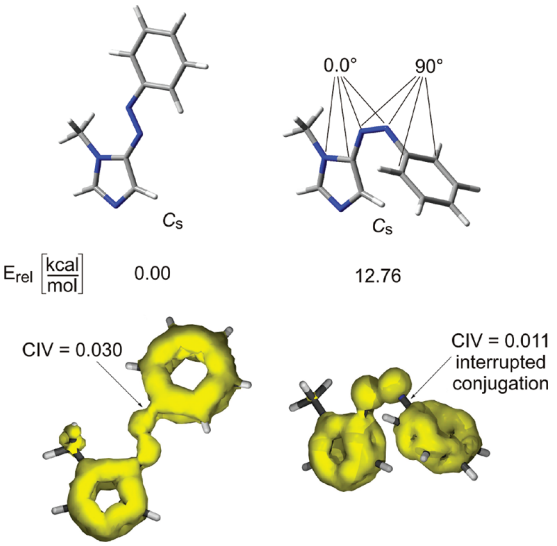

Figure 2. (Top) DFT (B3LYP/6-31G*) calculated geometries (dihedral angles are defined each by the four atoms indicated) and relative energies (kcal mol^{-1}) of the most stable conformations of the *trans* and *cis* configuration of 1-methyl-5-phenylazoimidazole **7**. (Bottom) ACID plots of the structures above (only π electrons are included, isosurface value 0.023). Critical isosurface values (CIV) indicate the ACID value at the weakest point in conjugation.

density of delocalized electrons including the imidazole ring, the phenyl ring, and the azo unit, whereas the *cis* isomer exhibits a distinctly isolated phenyl ring.

The light-induced switching of conjugation might be interesting for a number of applications (e.g., coupling of radical centers[33] or control of the donor strength of a heterocyclic transition metal ligand[34]). Because of the difference in conjugation, the $\pi-\pi^*$ absorptions are well separated in both isomers (λ_{max} *cis*-**7**: 312 nm, *trans*-**7**: 362 nm, Figure 3).

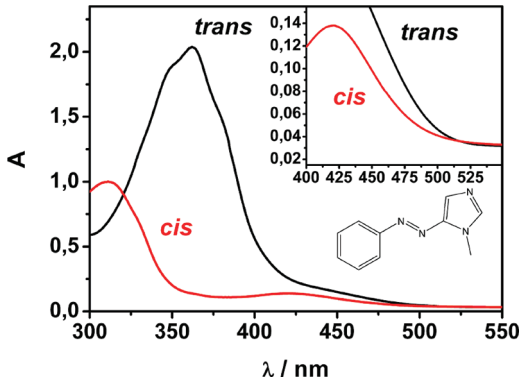

Figure 3. Absorption spectra of 1-methyl-5-phenylazoimidazole (**7**) in toluene (0.1 mM). Black curve: pure *trans*-isomer. Red curve: photostationary equilibrium at 365 nm (98% *cis*- and 2% *trans*-isomer).

There is strong absorption of the *trans* isomer at 365 nm and very little in the *cis* form. This is probably the reason for the very efficient conversion from *trans*- to *cis*-**7** at this wavelength. Similar to azobenzenes with electron-donating substituents,[2] the $\pi-\pi^*$ transitions in our azoimidazoles are red-shifted (**4**: 340 nm, **5**, **6**: 336 nm, and **7**: 362 nm) with respect to the corresponding transition in parent azobenzene (314 nm) and partially overlap with the n$-\pi^*$ transitions. This is in contrast to azobenzenes where the $\pi-\pi^*$ (used for *trans*→*cis* isomerization) and the n$-\pi^*$ transitions (*cis*→*trans*) are clearly separated. Therefore, the photochemical back switching which is usually performed with visible light of about 450 nm in azobenzenes and azopyridines is inefficient in our azoimidazoles. The photostationary equilibrium of **7** at 455 nm contains 45% *trans* and 55% *trans* at 297 nm. Complete conversion to the *trans* configuration is obtained upon heating to 70 °C for several hours.

CONCLUSION

With the 5-phenylazoimidazoles, we present a new class of photoswitchable azoheterocycles. A novel type of azo coupling, the reaction of lithiated imidazole with benzene diazonium salts provides access to these azo compounds. Conversion from the *trans* to the *cis* isomer by irradiation with 365 nm is superior (95−98%) to most azobenzenes and azopyridines. Moreover, *cis*-**7** exhibits a very slow thermal back-isomerization to the *trans* form.

EXPERIMENTAL SECTION

1-Dimethylsulfamoyl-5-phenylazoimidazole (4). 1-*N*,*N*-Dimethylsulfamoylimidazole[19] (5.00 g, 28.5 mmol) was dissolved under nitrogen in dry THF (150 mL) and cooled to −78 °C. Then, *n*-BuLi (2.5 M in hexane, 11.4 mL, 28.5 mmol) was injected slowly, and the solution was stirred at −78 °C for 30 min. Dimethylthexylsilyl chloride (6.15 mL, 31.3 mmol) was then injected and the cooling bath removed and stirred at room temperature overnight. The solution was again cooled to −78 °C, *n*-BuLi (2.5 M in hexane, 12.5 mL, 31.3 mmol) was injected slowly, and the mixture was stirred at −78 °C for another 30 min. Benzenediazonium tetrafluoroborate[35] (5.47 g, 31.3 mmol) was added under nitrogen, the cooling bath was removed, and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with diluted aq $NaHCO_3$, and the organic layer separated and dried over $MgSO_4$. The solvent was removed in vacuo to give 12.2 g of a deep red oil, which was used further without purification. The oil (1.5 g) was stirred for 1 h with tetrabutylammonium fluoride solution (7.0 mL, 1 M in THF) and a spatula tip of cesium fluoride in THF (10 mL) at room temperature. The solution was treated with diluted aq $NaHCO_3$ and then extracted with DCM (3 × 50 mL). The organic layer was separated and dried over $MgSO_4$, and the solvent was evaporated in vacuo. Purification by chromatography on silica gel using DCM/EtOAc 9:1 as eluent (R_f = 0.46) gave **4** as a red solid (535 mg, 54%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.84 (m, 2H), 7.50 (m, 4H), 2.98 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 145.0, 140.9, 131.7, 129.3, 123.0, 118.7, 38.4; HRMS (EI) calcd for $C_{11}H_{13}N_5SO_2$ 279.07901, found 279.07892; UV−vis (toluene) λ_{max} (lg ε) = 340 nm (4.414); mp 91 °C.

4(5)-Phenylazoimidazole (1). 1-Dimethylsulfamoyl-5-phenylazoimidazole (**4**) (300 mg, 1.07 mmol) was stirred for 1 h with EtOH/concd HCl 4:1 (50 mL) under reflux and neutralized after cooling with 40% KOH (pH ∼10, ice bath). The solution was extracted with $CHCl_3$ (3 × 50 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was evaporated in vacuo. Purification by chromatography on silica gel using EtOAc as eluent (R_f = 0.27) gave **1** as an orange solid (185 mg, quant): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 3H), 7.80 (d, J = 1.0 Hz, 1H), 7.48 (m, 2H), 7.43 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 136.3, 130.6, 129.1, 122.5; HRMS (EI) calcd for $C_9H_8N_4$ 172.07489, found 172.07538; UV−vis (toluene) λ_{max} (lg ε) = 347 nm (4.335); mp 149 °C.

1-Methyl-4-phenylazoimidazole (5). 4(5)-Phenylazoimidazole (**1**) (200 mg, 1.16 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. Then, 60% sodium hydride in mineral oil (51.0 mg, 1.28 mmol) was added portionwise. The solution was allowed to warm to room temperature and stirred for 10 min. After the solution was cooled to 0 °C, methyl iodide (80.0 μL, 1.28 mmol) was added and the solution stirred for 3 h at room temperature. Water (10.0 mL) was added and the solution extracted with DCM (3 × 30 mL). The

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combined organic layers were dried over $MgSO_4$, and the solvent was evaporated in vacuo. Purification by chromatography on silica gel using acetone as eluent (R_f = 0.69) gave **5** as an orange solid (140 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (m, 2H), 7.54 (d, J = 1.3 Hz, 1H), 7.47 (m, 3H), 7.41 (m, 1H) 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 153.0, 138.1, 130.3, 128.9, 122.7, 119.9, 34.1; MS (EI) m/z 186 (M^+), 158, 109; UV−vis (toluene) λ_{max} (lg ε) = 336 nm (4.169); mp 167−170 °C. Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.60; H, 5.57; N, 29.83.

1-Trityl-4-phenylazoimidazole (6). 4(5)-Phenylazoimidazole (**1**) (213 mg, 1.24 mmol), trityl chloride (345 mg, 1.24 mmol), and triethylamine (172 μL, 1.72 mmol) were heated under reflux in acetonitrile (20 mL) for 3 h. The solvent was evaporated in vacuo and the orange precipitate dissolved in $CHCl_3$ (20 mL). The organic layer was washed with water (2 × 10 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated in vacuo. The orange solid was recrystallized from acetonitrile to give **6** as an orange solid (390 mg, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (m, 2H), 7.59 (d, J = 1.4 Hz, 1H), 7.55 (d, J = 1.2 Hz, 1H) 7.45 (m, 2H), 7.38 (m, 10H), 7.21 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 151.0, 150.9, 139.7, 137.2, 128.3, 127.7, 126.9, 126.4, 126.3, 120.6, 120.2, 74.3; MS (EI) m/z 414 (M^+), 243, 165, 141, 111; UV−vis (toluene) λ_{max} (lg ε) = 336 nm (4.141); mp 208 °C. Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.18; H, 5.61; N, 13.87.

1-Methyl-5-phenylazoimidazole (7). 1-Trityl-4-phenylazoimidazole (**6**) (300 mg, 724 μmol) was dissolved in dry DCM (5 mL), and methyl triflate (125 μL, 1.09 mmol) was added and stirred at room temperature for 16 h. Acetone/water 1:1 (20 mL) was added, and stirring was continued for 3 h. Then, concd aq $NaHCO_3$ (10 mL) was added, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue purified by chromatography on silica gel using ethyl acetate as eluent (R_f = 0.20) to give **7** as a thick orange oil (102 mg, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.66 (s, 1H), 7.59 (s, 1H), 7.49 (m, 2H), 7.45 (m, 1H), 3.98 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 153.0, 145.3, 140.3, 130.7, 129.1, 123.0, 122.4, 32.5; MS (EI) m/z 186 (M^+), 109; UV−vis (toluene) λ_{max} (lg ε) = 362 nm (4.411). Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.53; H, 5.38; N, 30.09.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{13}C NMR, and UV−vis spectra for compounds **1** and **4**−**7** and crystallographic data for compound **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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