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Near-Infrared Absorbing Azo Dyes: Synthesis and X-ray Crystallographic and Spectral Characterization of Monoazopyrroles, Bisazopyrroles, and a Boron−Azopyrrole Complex

Yan Li, Brian O. Patrick, and David Dolphin*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., V6T 1Z1, Canada

david.dolphin@ubc.ca

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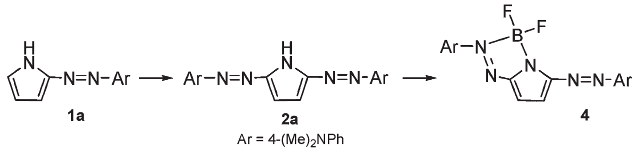

UV:	447 nm	575 nm	754 nm
N=N:	1.253(2) Å	1.283(2) Å	1.322(2) Å, 1.300(2) Å

Symmetric 2,5-bisazopyrroles **2(a−d)** were synthesized by a one-step reaction of substituted phenyl diazonium salts [R′(Ph)$N_2^+Cl^-$] [**a**, R′ = 4-N(CH_3)$_2$; **b**, R′ = 2-OH; **c**, R′ = 2-CO_2H; **d**, R′ = 4-NO_2] with pyrrole under basic conditions. Asymmetric 2,5-bisazopyrroles **3(a−d)** were synthesized by reacting substituted phenyl diazonium salts [R″(Ph)$N_2^+Cl^-$] (**a**, R″ = 4-OCH_3; **b**, R″ = H; **c**, R″ = 4-Br; **d**, R″ = 4-NO_2) with 2-(4-dimethylaminophenylazo)-1*H*-pyrrole (**1a**) under the same conditions. The reactions of **2a** with boron trifluoride and iodomethane provided a BF_2-azopyrrole complex of 1*H*-pyrrolo[2,1-*c*]-1,2,4,5-boratriazole (**4**) and 2,5-bisazo-1-methylpyrrole **5**. X-ray crystallographic and spectral analysis of **1a**, **2a**, **2b**, and **4** showed that **1a** has three crystal forms: 1a(I), **1a(II)**, and **1a(III)**, the latter two bearing a bicyclic ring system formed via intermolecular hydrogen bonding. Complex **4** was found to be the most planar due to a rigid trans-azo configuration and has the longest N=N bond distances (1.322 and 1.300 Å) and wavelength of maximum absorption (754 nm). The N=N bond distances increase in the sequence of monoazopyrrole [**1a(I)**: 1.253 Å], bisazopyrrole (**2a**: 1.283 Å), bisazopyrrole with intramolecular hydrogen bonding (**2b**: 1.293 and 1.293 Å), and the BF_2−azopyrrole complex. Their maximum absorptions shift bathochromically in the sequence of monoazopyrrole (**1a**: 443 nm), bisazopyrroles [**2(a−d)**, **3(a−d)**, **5**: 486−615 nm], and the BF_2−azopyrrole complex. These results are important for the design of near-infrared absorbing azo dyes and suggest an efficient path for the preparation of near-infrared absorbing azo dyes by effectively enhancing π-electron delocalization.

Introduction

Azo dyes are a class of compounds containing a N=N double bond and, due to their ability to absorb visible light, and ease of synthesis, have been extensively used in the textile, fiber, leather, paint and printing industries for more than a century.[1] Among the known azo dyes, five-membered heterocyclic azo dyes, such as azothiazole, azothiophene, azopyrrole, and azofuran, are important since they have pronounced bathochromic absorptions compared to azobenzene dyes[2] and are environmentally friendly.[3] Near-infrared absorbing azo dyes, based on five-membered heterocyclic rings, have been made effectively by using three methods: (1) introducing electron-donating or -accepting groups to the azo-linked aromatic ring to increase molecular

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donor−acceptor polarization;[4] (2) expanding the azo-linked aromatic ring from benzene to naphthalene and from thiazole to benzothiazole;[5] and (3) extending the conjugated N═N bond from monoazo to bisazo dyes to enhance molecular π-resonance effects.[6] The near-infrared absorbing azo heterocycles have been found to be useful as optical data carriers,[4e,4f,6b] thermal transfer recording media,[4c,5a,5b,6c] electrophotographic toners,[4b,4d,6f] and semiconductor lasers.[5d,6e]

While numerous syntheses and applications of five-membered heterocyclic azo dyes have been reported, studies on the relationship between molecular structure and color by theoretical and experimental methods have also received much interest. Most of the theoretical work addresses molecular donor−acceptor polarization,[7−9] with relatively less interest in the donor−acceptor polarization enhanced by π-resonance effects of expanded aromatic rings and extended N═N bonds.[9] Experimental studies with X-ray crystallography have been limited since it has been difficult to compare differences in crystallographic structures and the resulting change in color. In 2004, McNelis and co-workers[10] successfully investigated the relationship between the donor−acceptor polarization of azothiophenes and their colors using X-ray crystallography. 2-(4-Diethylaminophenylazo)thiophene has a N═N bond distance of 1.226 Å; when the strong electron-accepting tricyanovinyl group was introduced, the resulting products, 2-(4-diethylamino)phenylazo-5-tricyanovinylthiophene and 2-(4-tricyanovinyl)-phenylazo-5-diethylaminothiophene, exhibited N═N bond distances of 1.297 and 1.314 Å, with maximum absorptions at 719 and 708 nm, respectively. Regrettably, the relationship between π-resonance, planarity, and colors for five-membered heterocyclic azo dyes has not been explored theoretically nor via X-ray crystallography. In 2004, Centore and co-workers[11] investigated [4-di(hydroxyethyl)aminophenyl]azobenzenes containing a benzimidazole group. When molecular planarity was significantly improved by the insertion of a vinylene group between [4-di(hydroxyethyl)aminophenyl]azobenzene and benzimidazole, the λ_{max} was bathochromically shifted from 466 to 487 nm. This result indicated, not surprisingly, the importance of π-resonance effects on the bathochromic absorptions.

Most azo dyes are prepared via coupling of aromatic diazonium salts with a nucleophilic component. While this is true for 2,5-bisazathiophenes which are prepared from thiophen-2-yl diazonium salts,[12] the corresponding analogues of 2-aminothiophene[13] and 2,5-diaminothiophene[14] require multicomponent condensations; pyrrole, on the other hand, is more reactive than thiophene or even aniline (which is 10^{20} times more reactive than benzene). Few 2,5-bisazopyrroles have been reported[15−17] and we report here the coupling to pyrrole to produce 2,5-bis(arylazo)pyrroles.

A series of symmetric 2,5-bis(arylazo)-1*H*-pyrroles [**2(a−d)**] and asymmetric 2,5-bis(arylazo)-1*H*-pyrroles [**3(a−d)**] have been prepared and their maximum absorptions appear between 486 and 615 nm in dichloromethane, which are longer than that of monoazopyrrole **1a** (447 nm). When **2a** was reacted with iodomethane, symmetric 2,5-bis(arylazo)-1-methylpyrrole (**5**) was obtained, which has a similar absorption at 563 nm. However, when **2a** was reacted with boron trifluoride, the resulting boron−azopyrrole complex **4** displayed a near-infrared absorption at 754 nm. Comparisons of the X-ray crystallographic structures of **1a**, **2a**, **2b**, and **4** show that **4** is the most planar and has the longest N═N bond distance (1.322 and 1.300 Å), whereas **1a**, **2a**, and **2b** have N═N bond distances at 1.253 [**1a(I)**], 1.286 [**1a(II)**], 1.289 [**1a(III)**], 1.283 (**2a**), and 1.293 and 1.293 Å (**2b**).

Results and Discussion

Synthesis of 2,5-Bisazopyrrole and Derivatives. Following the general procedure to prepare azo dyes, substituted phenyl diazonium salts were formed by reacting aromatic amines [$R'PhNH_2$: R′ = 4-$N(CH_3)_2$, 4-OCH_3, 2-OH, H, 4-Br, 2-CO_2H, 4-NO_2] with sodium nitrite/aqueous HCl at temperatures lower than 0 °C. Neutralization with pyridine and treatment with a half equivalent of pyrrole in methanol gave symmetric bisazopyrroles **2(a−d)** [R′ = 4-$N(CH_3)_2$, 2-OH, 2-CO_2H, 4-NO_2] in 61−82% yields (Scheme 1, path 1). Monoazopyrrole **1a** was the major product when the 4-dimethylaminophenyl diazonium salt reacted with excess pyrrole under the same conditions (Scheme 1, path 2). Further reactions of **1a** with substituted phenyl diazonium salts provided asymmetric bisazopyrroles **3(a−d)** (R″ = 4-OCH_3, H, 4-Br, 4-NO_2)

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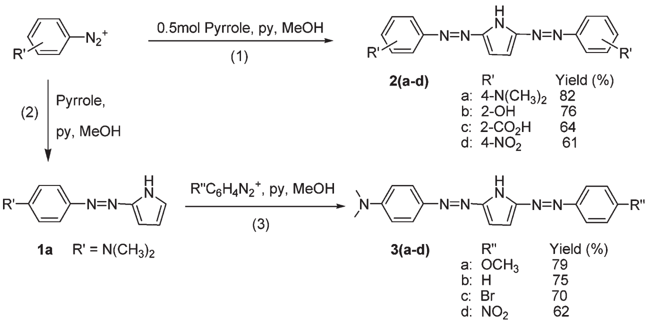
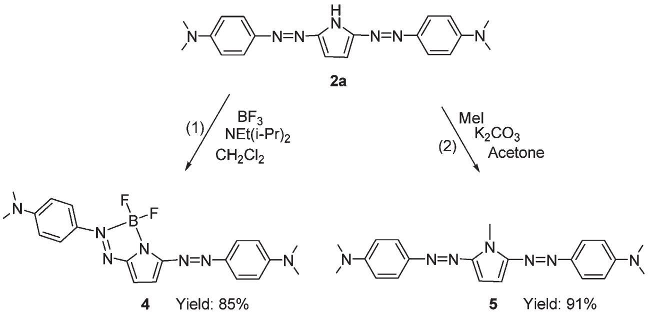
SCHEME 1. Synthesis of Symmetric 2,5-Bisazopyrroles 2(a−d) and Asymmetric 2,5-Bisazopyrroles 3(a−d)



SCHEME 2. Reactions of 2,5-Bisazopyrrole (2a) with Boron Trifluoride and Iodomethane



in 62−79% yields (Scheme 1, path 3). **1a** can be converted into 2-(4-dimethylaminophenylazo)-5-nitro-1*H*-pyrrole (**1b**) by nitrition at −50 °C.[18]

When **2a** was mixed with boron trifluoride and diisopropylethylamine, under nitrogen, and refluxed in dichloromethane for 1 h, the corresponding BF$_2$−azopyrrole complex **4** was formed in 85% yield (Scheme 2, path 1). Complex **4** was purified by chromatography and was found to be stable in nonprotic solvents such as acetone, tetrahydrofuran, acetonitrile, dichloromethane, benzene, etc., but unstable in protic solvents such as methanol. When **2a** was refluxed with iodomethane and sodium carbonate in acetone for 3 h, 2,5-bisazo-1-methylpyrrole **5** was obtained in 91% yield (Scheme 2, path 2).

While monoazopyrrole **1a** is yellow, these new bisazopyrroles [**2(a−d)**, **3(a−d)**, and **5**] are red to blue, and the boron−azopyrrole complex **4** is green in dichloromethane.

X-ray Crystal Structures. The structures of **1a**, **2a**, **2b**, and **4** were determined by X-ray crystallography and are shown in Figure 1. Their selected bond lengths and angles are listed in Table 1. Crystal data and structure refinements are summarized in the Supporting Information. While 2-phenylazo-1-vinylpyrrole (**6**)[19] and a macrocyclic 2,3-bisazopyrrole[16] have been reported with X-ray crystal structures, and some boron−azo complexes have been identified by NMR, IR, and MS spectra,[20,21] **1a**, **2a**, **2b**, and **4** are the first examples of monoazo-1*H*-pyrroles, 2,5-bisazo heterocycles (thiophene, pyrrole, and furan), and boron−azo complexes reported with X-ray crystal structures.

Monoazopyrrole **1a** has three forms within a unit cell: **1a (I)** shows no hydrogen bonding while **1a(II)** and **1a(III)** are both intermolecularly hydrogen bonded to each other between the nitrogen-1 of pyrrole and the nitrogen of an azo bond with N−H···N bond distances of 3.020 (N1···N7) and 3.087 Å (N3···N5). Compound **2a** has crystallographic mirror symmetry with identical H4n−N4−C9 and H4n−N4-C9* angles of 125.8°. Compound **2b** is slightly asymmetric, it has two intramolecular hydrogen bonds between the oxygen of the *o*-hydroxy groups and the nitrogen of the azo bond (=*N*-pyrrole) with O−H···N bond distances of 2.629 (O1···N2) and 2.601 Å (O2···N4). Intramolecular hydrogen bonding has been reported for *o*-hydroxy monoazo dyes, where the azophenol tautomers have H···N(azo) bond distances of 1.66−1.92 Å[22] and the hydrazoketone tautomers have H−N(hydrazone) bond distances of 0.84−1.24 Å.[22,23] The H···N bond distances of 1.839 (H1o···N2) and 1.819 Å (H2o···N4) indicate that **2b** principally exists as an azophenol tautomer. Intramolecular hydrogen bonding between N-1 of pyrrole and a nitrogen of the azo bond for **1a (I)**, **2a**, and **2b** should be very weak if it exists at all as the distances between the N-1 proton of pyrrole and the nitrogen of the azo bond [**1a(I)**: 2.592 Å; **2a**: 2.518 and 2.518 Å; **2b**: 2.458 and 2.568 Å] are slightly smaller than the sum of the van der Waals radii of hydrogen (1.20 Å) and nitrogen (1.50 Å) atoms.[24] Surprisingly, the N-1 proton of **1a(I)** is rotated away from the nitrogen of the azo bond, since the H9n−N9−C28 angle (127.7°) is larger than the H9n−N9−C25 angle (122.8°). For the BF$_2$−azopyrrole complex **4**, the nitrogen of one azo bond (Ar−*N*=) is coordinated to the N-1-BF$_2$ substituent at the pyrrole to form the novel structure 1*H*-pyrrolo[2,1-*c*]-1,2,4,5-boratriazole. The boron atom is sp^3 hybridized with an F1−B1−F2 angle (112.0°) divided by the B1/N2/N3/C9/N4 plane. The B−N bond distances are 1.537 (B1−N4) and 1.646 Å (B1−N2).

The structure of **1a(I)** is nearly planar, where the dihedral angle between the pyrrole and phenyl (C29/C30/C31/C32/C33/C34) planes is only 5.36°. As shown by side-view drawings in Figure 2, bisazopyrrole **2a** is less coplanar and butterfly like, with identical dihedral angles between the pyrrole and phenyl planes (C3/C4/C5/C6/C7/C8 and C3*/C4*/C5*/C6*/C7*/C8*) being 16.59°, which are larger than the dihedral angles of the phenyl planes in bisazo aromatic dyes (2.3−14.1°).[25] Intramolecular hydrogen-bonded **2b** is slightly ruffled, with the angles of the corresponding two

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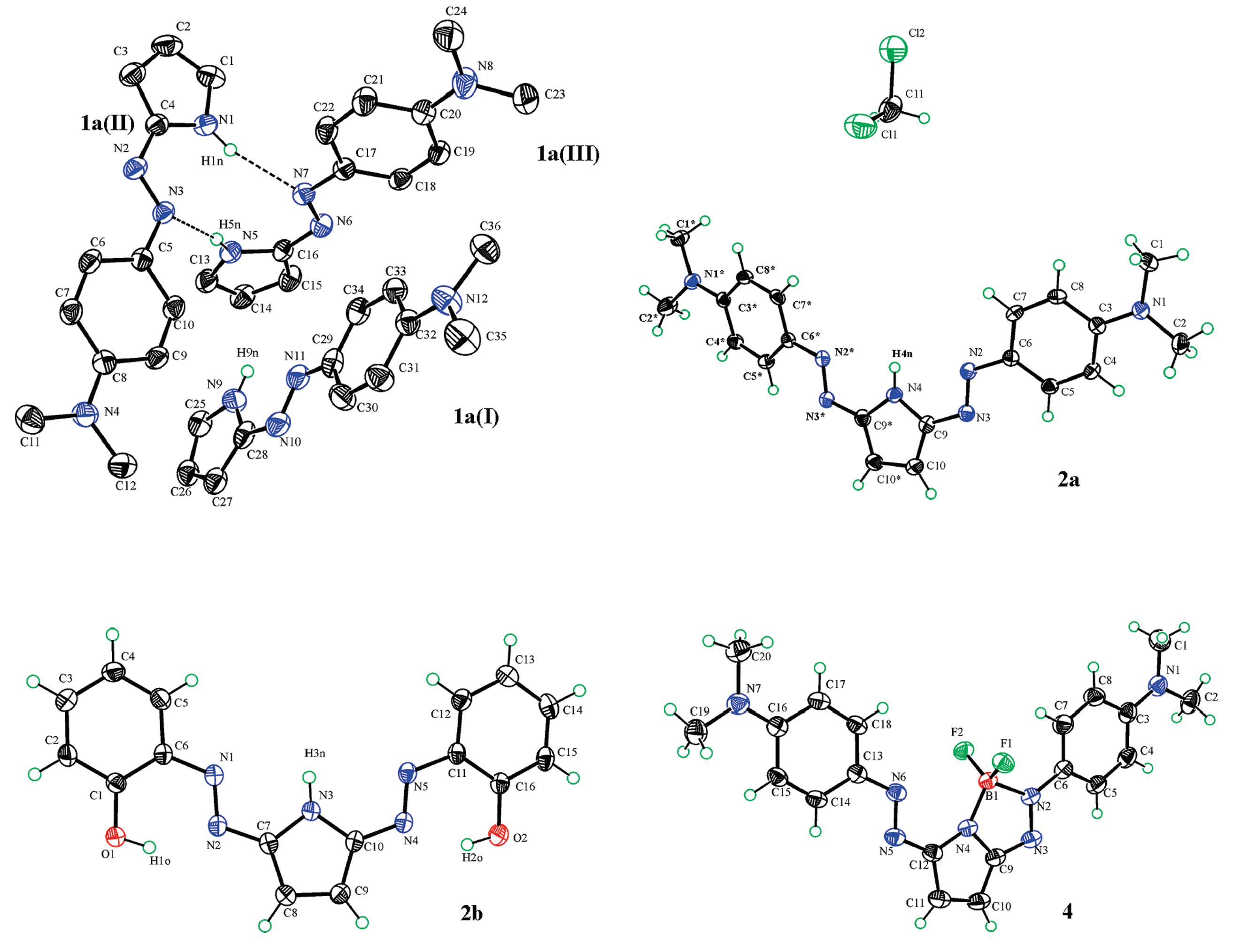

FIGURE 1. ORTEP views of the structures **1a**, **2a**·CH_2Cl_2, **2b**, and **4** (hydrogen atoms of **1a** are not shown).

TABLE 1. Selected Bond Distances (Å) and Angles (deg) of the Structures 1a, 2a·CH_2Cl_2, 2b, and 4

	1a(I)	**1a(II)**	**1a(III)**	**2a·CH_2Cl_2**	**2b**	**4**
H−N(pyrrole)	0.84(2)	0.90(2),	0.88(2)	0.84(3)	0.87(2)	
B−N(pyrrole,azo)						1.537(2), 1.646(2)
H···N(azo)		2.142	2.226		1.839, 1.819	
N−N	1.253(2)	1.286(2)	1.289(2)	1.283(2)	1.293(1), 1.293(1)	1.300(2), 1.322(2)
N(azo)−C(pyrrole)	1.42692)	1.386(2)	1.390(2)	1.380(2)	1.379(2), 1.380(2)	1.361(2), 1.377(2),
N(azo)−C(phenyl)	1.453(2)	1.423(2)	1.420(2)	1.404(2)	1.408(2), 1.412(2)	1.392(2), 1.398(2)
N−N−C(pyrrole)	110.9(2)	114.2(1)	113.8(1)	113.4(1)	113.1(1), 114.2(1)	112.5(1), 106.7(1),
N−N−C(phenyl)	112.1(2)	114.8(1)	115.0(1)	113.6(1)	116.1(1), 115.0(1)	114.4(1), 119.9(1)
X(B,C)−N4-C						143.2(1), 109.8(1), 106.9(1)
X(B,N)−N2-Y(C,N)						113.8(1), 126.3(1), 119.9(1)

planes being 5.66° (pyrrole and C1/C2/C3/C4/C5/C6 plane) and 6.43° (pyrrole and C11/C12/C13/C14/C15/C16 plane). Significantly, complexation improves the planarity of bisazopyrrole molecules; complex **4** is the most planar where the dihedral angles between the pyrrole and phenyl planes are 4.73° (pyrrole and C3/C4/C5/C6/C7/C8 plane) and 3.53° (pyrrole and C13/C14/C15/C16/C17/C18 plane). The mean deviations of carbon and nitrogen atoms from the π-delocalized skeletons containing azo, phenyl, and pyrrole groups are 0.047 Å in **1a**, 0.203 Å in **2a**, 0.065 Å in **2b**, and 0.045 Å in **4**. The small proton chemical shift differences of **2a** between 25 and −80 °C further indicate that the torsion angles between the aromatic planes do not significantly change [0.048, 0.096, 0.048, 0.087, and 0.044 ppm for *H*N (pyrrole), *H*C (benzene), *H*C (pyrrole), *H*C (benzene), and H_3C, respectively; see the Supporting Information].

All configurations for N=N−C(pyrrole) are in a trans-cis form. **1a(I)** exhibits a N=N bond distance of 1.253 Å, which is longer than those of simple monoazo dyes with thiophene (1.226 Å)[10] and shorter than those of **6** with enhanced π-resonance effects (1.271 Å)[19] and monoazothiophenes with electron-withdrawing groups (1.297−1.314 Å).[10] Inter- and intramolecular hydrogen bonds and the second azo bond extend the N=N bond distances to 1.286 Å for

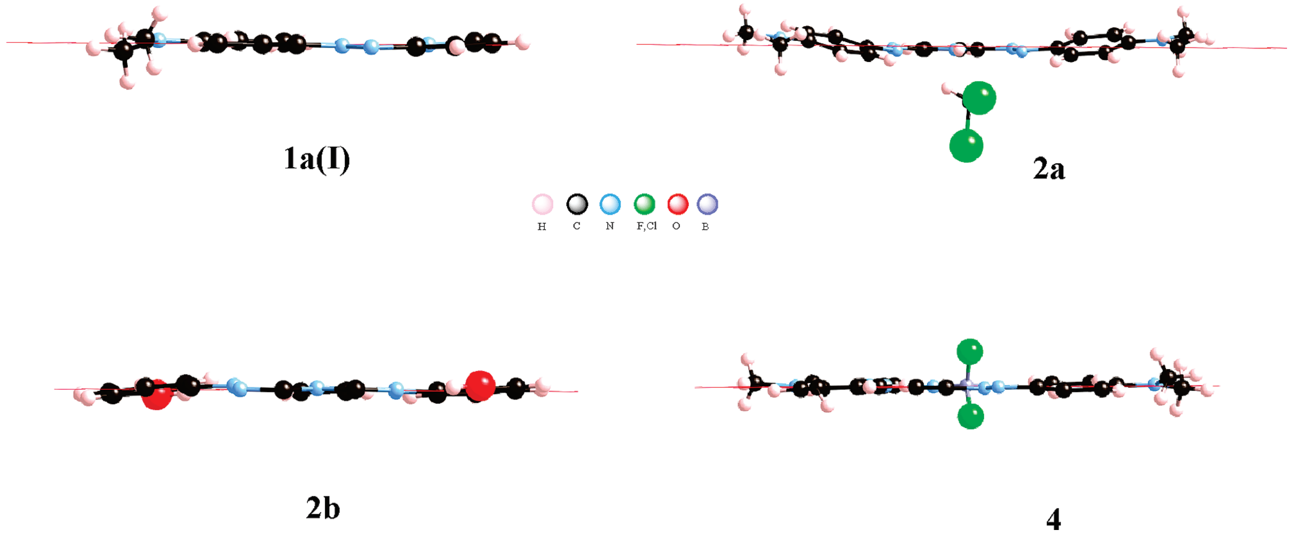

FIGURE 2. Side views of the structures of **1a(I)**, **2a**, **2b**, and **4**.

TABLE 2. Absorption Data of Azopyrroles in Dichloromethane and Methanol

compds	λ_{max} (log ε) in CH_2Cl_2	λ_{max} (log ε) in MeOH
1a	447 (4.79)	443
1b	530	498
2a	575 (4.77)	574 (4.79)
2b	519 (4.62)	507 (4.66)
2c	486	466 (4.64)
2d	490 (4.60)	487 (4.57)
3a	548 (4.69)	543 (4.74)
3b	558 (4.69)	543 (4.71)
3c	572 (4.68)	554 (4.71)
3d	615 (4.69)	589 (4.70)
4	754 (4.78)	
5	563 (4.81)	580

1a(II), 1.289 Å for **1a(III)**, 1.283 Å for **2a**, and 1.293 and 1.293 Å for **2b**. The boron−azopyrrole complex **4** has distinguishingly long N=N bond lengths. The free N=N bond distance is 1.300 Å and the rigid N=N bond distance is 1.322 Å, longer than the calculated N−N bond distance for 2-arylhydrazone−pyrrole structures (1.316 Å).[8] In contrast, **1a(I)** clearly has long N−C(pyrrole) and N−C(Ar) bond distances. The N−C(pyrrole) bond distances are 1.426 Å for **1a(I)**, 1.386 Å for **1a(II)**, 1.390 Å for **1a(III)**, 1.380 Å for **2a**, 1.391 and 1.388 Å for **2b**, and 1.361 and 1.377 Å for **4**, and the N−C(Ar) bond distances are 1.453 Å for **1a(I)**, 1.423 Å for **1a-(II)**, 1.420 Å for **1a(III)**, 1.404 Å for **2a**, 1.408 and 1.412 Å for **2b**, and 1.398 and 1.392 Å for **4**, decreasing in the sequence of monoazo, bisazo, and boron−azo complex, suggesting that complex **4** has the best π-electron delocalization.

UV−Vis Absorption Spectra of 2,5-Bisazopyrrole and Derivatives. The maximum absorptions of azopyrroles **1(a,b)**, **2-(a−d)**, **3(a−d)**, **4**, and **5** are listed in Table 2. For monoazo dyes, the visible absorption spectra are dominated by molecular donor−acceptor polarization. 2-(4-Dimethylaminophenyl)azo-1-*H*-pyrrole (**1a**) has a maximum absorption at 447 nm in dichloromethane or 443 nm in methanol, longer than those for (4-dimethylaminophenyl)azobenzene (408 nm)[26] and 2-(4-nitrophenyl)azo-1-*H*-pyrrole (420 nm),[27] which indicate that pyrrole acts as an effective acceptor in 2-arylazopyrrole chromophores. When the donor−acceptor polarization of **1a** is increased by introducing an electron-accepting nitro group into the 5-position of the pyrrole, the maximum absorption of **1b** is bathochromically shifted to 530 nm in dichloromethane and to 498 nm in methanol. Furthermore, when the π-resonance is enhanced by extending the monoazopyrrole to bisazopyrroles, asymmetric 2,5-bisazopyrroles **3a**, **3b**, **3c**, and **3d** have their maximum absorptions at 548, 558, 572, and 615 nm in dichloromethane and at 543, 543, 554, and 589 nm in methanol, respectively. The maximum absorption shifts bathochromically along with the increase in the electron-accepting ability of substituents in the sequence of *p*-OCH_3 (**3a**) < *p*-H (**3b**) < *p*-Br (**3c**) < *p*-NO_2 (**3d**), consistent with an increase in molecular donor−acceptor polarization. Note that the difference of the maximum absorptions of bisazopyrroles from **3b** to 3d is smaller than that of monoazopyrroles from **1a** to **1b**. Symmetric 2,5-bisazopyrroles **2a**, **2b**, **2c**, **2d**, and **5** also exhibit maximum absorptions at 575, 519, 486, 490, and 563 nm in dichloromethane and at 574, 507, 466, 487, and 580 nm in methanol, respectively, larger than those of **1a**. However, the maximum absorption shifts bathochromically along with the increase of the electron-donating ability of substituents on both sides in the sequence *p*-$N(CH_3)_2$ (**2a**) > *o*-OH (**2b**) > *p*-NO_2 (**2d**) > *o*-CO_2H (**2c**).

Typically, as shown in Figure 3 for **3a** and **3c**, the maximum absorption peaks for some bisazopyrroles overlap with a minor absorption peak. Similar spectral characteristics have been found for *o*-hydroxy azo dyes and reflect the azohydrazone tautomeric equilibria in solution,[28] where the absorption peaks to the red belong to the hydrazone tautomer and the other to the azo tautomer. Similar tautomeric equilibria, through intramolecular N(azo)···H···N (pyrrole) bonding, should exist for monoazo- and bisazo-1*H*-pyrroles as depicted in Scheme 3. The positions of tautomeric equilibria are affected by solvents and substituents; in addition, protic solvents can weaken the intramolecular

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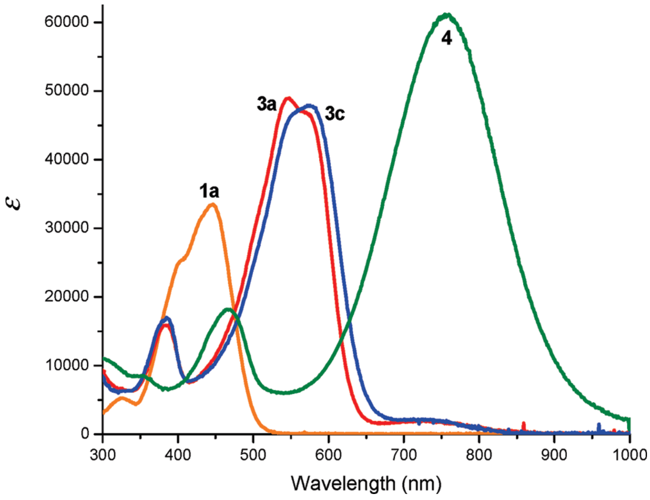


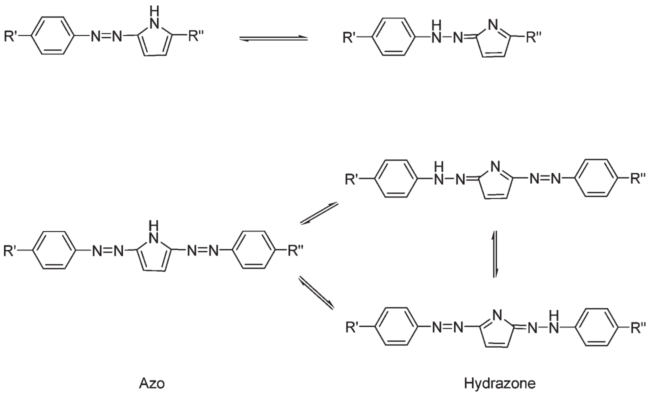
FIGURE 3. Absorption spectra of **1a** (orange line), bisazopyrrole **3a** (red line) and **3c** (blue line), and boron−azopyrrole complex **4** (green line) in dichloromethane.

hydrogen bonding and shift the equilibrium toward the azo tautomer.

For dichloromethane solutions of **3c** and **3d**, minor absorption peaks appear as shoulders on the blue side of the maximum absorption peaks, and tend to strengthen with a decrease in the electron-accepting ability of substituents in the sequence of **3b** (H) > **3c** (Br) > **3d** (NO_2). In contrast, for **2a** and **3a**, the minor absorption peaks appear as a shoulder on the red side of the maximum absorption peaks, and tend to weaken with an increase in the electron-donating ability of substituents in the sequence **3a** (OCH_3) < **3b** (H). Compared to those in dichloromethane, the maximum absorptions in methanol solutions show large hypsochromic shifts of 15 nm for **3b**, 18 nm for **3c**, 26 nm for **3d**, and 32 nm for **1b**, versus small shifts of 1 nm for **2a**, 3 nm for **2d**, 4 nm for **1a**, and 5 nm for **3a**. The hypsochromic shifts of the maximum absorptions by 12 nm for **2b** and 20 nm for **2c** are due to the disruption of the intramolecular N(azo)···H···O bonding. These spectral characteristics indicate that the hydrazone tautomers predominate in dichloromethane solution for monoazo- and unsymmetric 2,5-bisazo-1*H*-pyrroles with strong donor−acceptor polarization, such as **1b**, **3b**, **3c**, and **3d**, and the azo tautomers are predominant for monoazo- and 2,5-bisazo-1*H*-pyrroles with non- and weak donor−acceptor polarization, such as **1a**, **2a**, **2b**, **2d**, and **3a**, which are consistent with the X-ray crystal structures. An attempt to capture the hydrazone tautomer by reacting **2a** with MeI failed; only 2,5-bisazo-1-methylpyrrole **5** was isolated in high yield. The spectrum of **5** in dichloromethane also has a minor absorption peak appearing as a shoulder on the red side of the maximum absorption peak, similar to that of 2-arylazo-1-vinylpyrroles.[19]

Significantly, the boron−azopyrrole complex **4** has its maximum absorption at 754 nm in dichloromethane (Figure 3), bathochromically shifted by 179 nm relative to that of **2a**. This presumably results from significant π-electron delocalization in the planar structure dominated by complexation of the electron-withdrawing BF_2 group. Since symmetric bisazobenzidines[28] and BF_2 complexes of dipyrromethene[29] and tetraarylazadipyrromethene[30] have been investigated as photosensitizers for photodynamic therapy, the BF_2−azo complex described here is a potential photosensitizer in this field.

SCHEME 3. Tautomerization Proposed for Monoazo- and Bisazo-1*H*-pyrroles



Conclusion

Symmetric 2,5-bisazopyrroles **2(a−d)** and **5**, asymmetric 2,5-bisazopyrroles **3(a−d)**, and the novel BF_2−azopyrrole complex of 1*H*-pyrrolo[2,1-*c*]-1,2,4,5-boratriazole (**4**) have been synthesized and fully characterized. The near-infrared absorption of BF_2−azo complex **4** is dominated by π-resonance effects which was achieved by extending the conjugation around the N=N bond and forming a rigid azo configuration. These results are important for the design of near-infrared absorbing azo dyes and provide an effective and simple method to synthesize such dyes by enhancing π-electron delocalization. The synthesis of proton-inert complexes of 1*H*-pyrrolo[2,1-*c*]-1,2,4,5-boratriazoles and their application as photosensitizers for photodynamic therapy are under progress.

Experimental Section

Preparation of 2,5-Bis(4-dimethylaminophenylazo)-1*H*-pyrrole (2a). To a suspension of the aromatic amine (8.0 mmol) in water (15 mL) was added concentrated hydrochloric acid (24 mmol, 2 mL) until the mixture was homogeneous. The solution was cooled and kept at 0−5 °C in an ice bath and diazotized by addition of a solution of sodium nitrite (8.2 mmol, 0.566 g) in water (5 mL), followed by stirring for 30 min at 0−5 °C. To a solution of pyrrole (4 mmol, 0.28 mL) and pyridine (50 mmol, 4 mL) in methanol (150 mL) was slowly added a solution of the diazonium salt at 0−5 °C. The resulting mixture was stirred for 5 h and then evaporated under vacuum to dryness. The residues were purified by column chromatography, eluting with a mixture of dichloromethane and hexane (1:1). Yield 82%. Mp 228−229 °C. Anal. Calcd for $C_{20}H_{23}N_7\cdot{}^1/_3$ CH_2Cl_2 (solvent of crystallization determined by NMR): C, 62.66; H, 6.12; N, 25.16. Found: C, 62.41; H, 6.52; N, 25.52. ^{1}H NMR (CD_2Cl_2) δ 9.77 (s, 1H), 7.80 (s, 4H), 6.88 (s, 2H), 6.77 (d, $J = 8.9$ Hz, 4H), 3.10 (s, 12H). ^{1}H NMR ($CDCl_3$) δ 9.77 (s, 1H),

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7.78 (d, J = 8.3 Hz, 4H), 6.89 (s, 2H), 6.73 (d, J = 8.3 Hz, 4H), 3.09 (s, 12H). ^{1}H NMR (CD_3OD) δ 7.74 (d, J = 9.1 Hz, 4H), 6.81 (s, 2H), 6.80 (d, J = 9.2 Hz, 4H), 3.07 (s, 12H). ^{13}C NMR (CD_2Cl_2) δ 152.7, 146.5, 144.5, 124.9, 114.3, 112.3, 40.3. IR ν (N=N) 1377 cm^{-1}. UV−vis (1.03×10^{-5} M, CH_2Cl_2) λ_{max} (log ε) 411 (4.34), 575 (4.77). UV−vis (1.41×10^{-5} M, CH_3OH) λ_{max} (log ε) 407 (4.22), 574 (4.79). EI MS m/z 361 (M$^+$).

Preparation of 2-(4-Dimethylaminophenylazo)-1*H*-pyrrole (1a).[31] **1a** was prepared by using the same procedure as for **2a** but with 2 equiv of pyrrole and it was purified by column chromatography eluting with a mixture of dichloromethane and hexane (1:2). Mp 147−148 °C. ^{1}H NMR ($CDCl_3$) δ 9.33 (s, 1H), 7.75 (d, J = 9.2 Hz, 2H), 6.84 (d, J = 3.6 Hz, 1H), 6.79 (s, 1H), 6.73 (d, J = 9.2 Hz, 2H), 6.32 (t, J = 3.2 Hz, 1H), 3.03 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 151.8, 146.3, 143.6, 124.1, 119.9, 112.1, 112.0, 111.0, 40.6. IR ν (N=N) 1377 cm^{-1}. UV−vis (1.64×10^{-5} M, CH_2Cl_2) λ_{max} 447 (4.52). UV−vis (CH_3OH) λ_{max} (log ε) 443. EI MS m/z 214 (M$^+$).

Preparation of 2-(4-Dimethylaminophenylazo)-5-nitro-1*H*-pyrrole (1b). This compound was prepared according to the literature[18] by nitration of **1a** with a mixture of acetic anhydride and nitric acid at −50 °C. Dark crystals. Yield 32%. Mp 208−209 °C. ^{1}H NMR ($CDCl_3$) δ 9.93 (s, 1H), 7.80 (d, J = 9.2 Hz, 2H), 7.17 (d, J = 4.4 Hz, 1H), 6.74 (d, J = 4.0 Hz, 1H), 6.20 (d, J = 8.97 Hz, 2H), 3.11 (s, 6H). ^{13}C NMR ($CDCl_3$) 153.5, 146.7, 143.4, 126.1, 114.9, 112.8, 111.9, 110.5, 40.5. IR:ν (N=N) 1376 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} 530. UV−vis (CH_3OH) λ_{max} 498. HR-EI MS (M$^+$) m/z calcd for $C_{12}H_{13}N_5O_2$ 259.1069, found 259.1071.

Preparation of 2-(4-Methoxyphenylazo)-5-(4-dimethylaminophenylazo)-1*H*-pyrrole (3a). **3a** was prepared by using the same procedure as for **2a** but with 1 equiv of **1a** instead of pyrrole and purified by column chromatography eluting with a mixture of dichloromethane and hexane (2:3). Yield 79%. Mp 166−167 °C. Anal. Calcd for $C_{19}H_{20}N_6O$: C, 65.50; H, 5.79; N, 24.12. Found: C, 65.15; H, 5.85; N, 24.39. ^{1}H NMR ($CDCl_3$) δ 9.74 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.01−6.95 (m, 3H), 6.92 (d, J = 4.1 Hz, 1H), 6.76−6.71 (m, 2H), 3.87 (s, 3H), 3.08 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 161.6, 152.4, 147.6, 146.7, 145.5, 144.2, 125.0, 124.3, 116.2, 114.6, 114.0, 112.0, 55.8, 40.5. IR ν (N=N) 1380 cm^{-1}. UV−vis (1.31×10^{-5} M, CH_2Cl_2) λ_{max} (log ε) 384 (4.20), 548 (4.69). UV−vis (1.24×10^{-5} M, CH_3OH) λ_{max} (log ε) 382 (4.18), 543 (4.74). EI MS m/z 348 (M$^+$).

Preparation of 2,5-Bis(4-dimethylaminophenylazo)pyrrole-1-boron Difluoride (4). To a solution of **2a** (0.28 mmol, 100 mg) and diisopropylethylamine (4.2 mmol, 0.73 mL) in dry dichloromethane (50 mL) was slowly added boron trifluoride diethyl etherate (1.4 mmol, 0.18 mL) under nitrogen. The resulting solution was refluxed for 1 h and then evaporated under vacuum to dryness. The residue was purified by column chromatography eluting with dichloromethane and hexane (1:1) to give a green product. Yield 85%. Mp 205−206 °C. Anal. Calcd for $C_{20}H_{22}BF_2N_7$: C, 58.70; H, 5.42; N, 23.96. Found: C, 58.99; H, 5.59; N, 24.14. ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 9.20 Hz, 4H), 6.94 (s, 2H), 6.72 (d, J = 9.30 Hz, 4H), 3.10 (s, 12H). ^{11}B NMR ($CDCl_3$) δ 3.62. IR ν (N=N) 1422 cm^{-1}. UV−vis (1.12×10^{-5} M, CH_2Cl_2) λ_{max} (log ε) 466 (4.26), 754 (4.78). ESI MS m/z 409 (M$^+$).

Preparation of 2,5-Bis(4-dimethylaminophenylazo)-1-methylpyrrole (5). To a mixture of **2a** (0.28 mmol, 100 mg) and potassium carbonate (1.68 mmol, 232 mg) in dry acetone (50 mL) was added iodomethane (0.84 mmol, 52 μL) under nitrogen. The resulting solution was refluxed for 3 h and then evaporated under vacuum to dryness. The residue was purified by column chromatography eluting with a mixture of dichloromethane and hexane (1:1). Yield 91%. Mp 242−243 °C. Anal. Calcd for $C_{21}H_{25}N_7$: C, 67.18; H, 6.71; N, 26.11. Found: C, 66.87; H, 6.70; N, 26.28. ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 8.98 Hz, 4H), 6.73 (d, J = 9.0 Hz, 6H), 4.18 (s, 3H), 3.07 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 151.8, 148.4, 145.2, 124.4, 112.0, 101.0, 40.6, 29.5. IR ν (N=N) 1378 cm^{-1}. UV−vis (1.24×10^{-5} M, CH_2Cl_2) λ_{max} (log ε) 563 (4.81), 767 (4.13). UV−vis (CH_3OH) λ_{max} 580. EI MS m/z 375 (M$^+$).

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Supporting Information Available: Experimental procedures, NMR and UV−vis spectra, and detailed X-ray crystallographic characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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