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Synthesis and Characterization of 3-Cyano- and 3-Nitroformazans, Nitrogen-Rich Analogues of β-Diketimine Ligands

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The synthesis and characterization of several formazans containing strong electron-withdrawing substituents (cyano and nitro) in the 3 position of the ligand backbone are described. Reactions of aryldiazonium cations with the conjugated bases of either cyanoacetic acid or nitromethane lead to 1,5-diaryl-3-cyano- or 3-nitroformazans, respectively. When these reactions are carried out in aqueous conditions, the range of aromatic groups is limited by the stability of the diazonium salt. However, 3-nitroformazans containing bulky substituents on the nitrogen atoms (2,6-dimethylphenyl, 2,4,6-trimetyhlphenyl, 2,6-diisopropylphenyl, and 3,5-ditert-butylphenyl) could be made by performing the reactions under nonaqueous and anhydrous conditions. NMR and electronic spectroscopic studies indicate that the 3-nitroformazans exist exclusively as closed (*trans-syn, s-cis*) isomers whereas the 3-cyanoformazans exist as mixtures of isomers which are substrate-dependent. The crystal structures of five of the formazans are presented: two 3-nitroformazans, both of which are closed, and three 3-cyanoformazans, two of which are closed and one of which adopts an open (*trans-syn*, *s-trans*) structure. Solid state (diffuse reflectance) spectroscopy has been employed to ascertain the isomeric preferences of the other formazans which could not be crystallographically characterized.

Introduction

Formazans (**1**) have been widely studied since 1941 and have been reported as far back as the 1890s.[1] These compounds have attracted interest mainly because of their intense colors; they are commonly used as dyes[2] and as redox-based staining agents for cell biology.[3] However, the chemical reactivity of formazans is largely unexplored. We are interested in developing the *inorganic* chemistry of formazans[4] based on their close structural relationship to β-diketimines **2**. In the past decade, the latter (as their conjugate bases, the diketimin*ates*) have become one of the most versatile and popular ancillary ligand platforms for main group and transition metal chemistry.[5] The coordination chemistry of formazans has been sporadically explored for over 60 years but remains essentially an undeveloped field;[6] many formazan complexes which have been reported have been incompletely characterized,[7] and in fact, the same can be said for many of the formazan derivatives themselves.

Many of the most popular β-diketimine ligands possess nitrogen substituents (R_1 and R_5) of considerable steric bulk, for example, 2,4,6-trimethylphenyl (Mes) and 2,6-diisopro-

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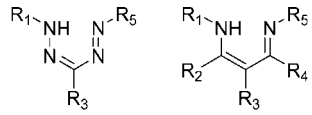


1 2

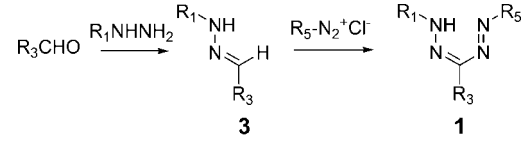
pylphenyl (Dipp). Complexes of bulky β-diketiminates have tended to have unusual structure and bonding environments and have also afforded highly active catalysts for a variety of chemical transformations. A survey of the >1000 known formazan derivatives[8] reveals that only *two* of these have even moderately bulky mesityl N_1/N_5 substituents,[9,10] and there are *no* examples of formazans with larger R_1 and R_5 groups. In this paper, we describe the synthesis and comprehensive (solution and solid state) characterization of formazans with cyano or nitro substituents in the 3 position of the formazan backbone and a range of aromatic groups as N substituents R_1 and R_5, in particular, derivatives with bulky nitrogen substituents.

Results and Discussion

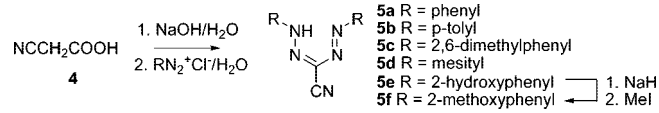
Synthesis. The most common method for making formazans is outlined in Scheme 1. In this route, condensation of a monosubstituted hydrazine with an aldehyde gives a hydrazone **3**, which under basic conditions adds to aryldiazonium cations to give the resulting formazan, **1**. This modular synthesis can be applied to a wide range of substituents, the only constraints being that R_5 = Ar and that the monosubstituted hydrazine R_1NHNH_2 be accessible. In the context of preparing formazans with bulky nitrogen substituents, however, this synthetic route is limiting because the required hydrazines are either unknown or very difficult to handle owing to their high reactivity.[11]

Another route to formazans which does not require hydrazine reagents is shown in Scheme 2. Acidic methylene compounds such as cyanoacetic acid (among others[1]) can be deprotonated and reacted with aryldiazonium salts in aqueous solution to give formazans **5** with cyano groups in the 3 position. This reaction proceeds via attack of the diazonium cation by the *in situ* generated carbanion to generate a hydrazone-type intermediate, which subsequently is deprotonated (either by the added base or initial carbanion) and then adds to a second equivalent of diazonium cation. The carboxyl group in **4** must also be lost, although it is not clear at what stage of the reaction this occurs. Using this method, we have prepared 3-cyanoformazans **5a**−**5f**, some of which have been previously reported but whose characterization is in all cases incomplete (see the Experimental Section). Formazan **5f** was also prepared by the selective methylation of the 2-hydroxy derivative **5e**. Attempts to prepare 3-cyanoformazans with nitrogen substituents larger

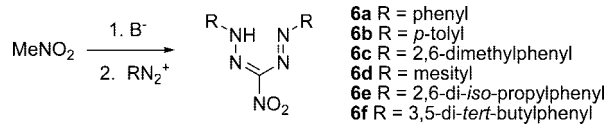
Scheme 1



Scheme 2



Scheme 3



than the Mes group failed owing to the instability of the corresponding diazonium cation in aqueous solution.

3-Nitroformazans can be synthesized using the same methodology as the one outlined for 3-cyanoformazans, using nitromethane in place of cyanoacetic acid (Scheme 3).[1,12] This route was employed for formazans **6a** and **6b**, which conveniently precipitate from solution. As was the case for the cyanoformazan system, the synthesis of 3-nitroformazans with bulkier N-aromatic groups could not achieved. In the nitromethane system, the presence of even *ortho*-methyl substituents (cf. **5c**, **5d**) causes this reaction to fail; the bis(2,6-dimethylphenyl) derivative **6c** has been made previously but in 1% yield.[13] However, we have found that the diazonium cations (as their BF_4^- salts) are stable enough in nonaqueous (anhydrous) conditions to couple with deprotonated nitromethane to afford 3-nitroformazans in fair to good yields. The tetrafluoroborate salts of the diazonium cations were generated from the corresponding anilines according to literature methods[14] and immediately reacted with deprotonated nitromethane. This route allows for the incorporation of bulky substituents onto the two nitrogen substituents of formazans for the first time.

Crystal Structures. There are fewer than 20 crystal structures of formazans. These can be divided into three structure types (Figure 1). Several formazans adopt the *trans-syn*, *s-cis* (hereafter referred to as "open") structure in which the NH proton bridges N1 and N5. This structure is favored by formazans with aryl or bulky alkyl substituents in the 3 position.[4,8,13,15] Formazans with relatively small R_3 groups (e.g., H, Me, Et, and SMe) crystallize in either the *trans-syn*,

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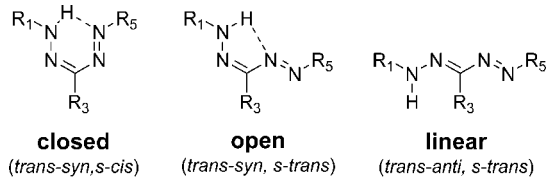

Figure 1. Formazan isomers.

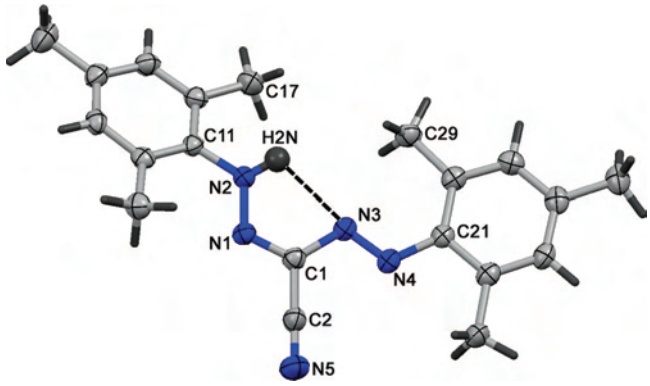

Figure 2. Molecular structure of **5d**. Thermal ellipsoids shown at 50% probability level.

s-trans ("open")[16,17] or *trans-anti*, *s-trans* ("linear")[8,17–19] configuration. Among the crystallographically characterized formazan derivatives there are no examples of 3-cyanoformazans and only one 3-nitroformazan (compound **6c**).[9,13] Crystal structures of three of the 3-cyanoformazans (**5d**, **5e**, and **5f**) and two of the 3-nitroformazans (**6b** and **6d**) have been determined (attempts to grow single crystals of the other derivatives suitable for X-ray studies were not successful). Table 1 summarizes the selected bond lengths and angles.

1,5-Bis(mesityl)-3-cyanoformazan, **5d** (Figure 2), adopts the open conformation in the solid state. The formazan backbone (N2−N1−C1−N3−N4) exhibits some bond-length alternation (N2−N1 1.325(2) Å, N3−N4 1.269(2) Å, N1−C1 1.304(2) Å, and N3−C1 1.392(2) Å), although the degree of alternation is somewhat attenuated compared to localized NN and CN single- and double-bond lengths. The mesityl substituent attached at N4 is nearly coplanar with the plane defined by the formazan (NNCNN) backbone (torsion angle of 7.3°), while the N2-mesityl ring is slightly more twisted (torsion angle = 29.8°).

In contrast to **5d**, the bis(*o*-hydroxyphenyl) and bis(*o*-methoxyphenyl) 3-cyanoformazans **5e** and **5f**, respectively, adopt the closed structure. The structure of **5e** is shown in Figure 3. The formazan backbone appears to be more delocalized than the corresponding structure of **5d** on the basis of the even smaller degree of bond length alternation in **5e** (N2−N1 1.3101(15) Å and N3−N4 1.2904(15) Å). The closed structure of **5f** (see the Supporting Information) shows no (within experimental error) bond length alternation (N2−N1, 1.292(3) and N3−N4, 1.296(3); N1−C1, 1.355(4); and N3−C1, 1.353(4) Å). These are consistent with the structures of other "closed" formazans, which also tend to show relatively small (sometimes almost negligible) bond-length alternation. The NH proton bridges N2 and N4; in addition to this expected intramolecular hydrogen bond, there is an intramolecular OH(2)−N3 hydrogen bond and an intermolecular (O1)H···N5 hydrogen bond to the cyano nitrogen of a neighboring molecule. As a result, the *intra*molecular hydrogen-bonded OH group adopts a syn orientation with respect to the NN bond nearest to it, while the *inter*molecularly hydrogen-bonded OH is anti. Both phenyl groups are nearly coplanar with the formazan backbone; the phenol ring attached to N2 is twisted by 3.8° and the phenol ring attached to N4 by 3.9° with respect to the formazan plane.

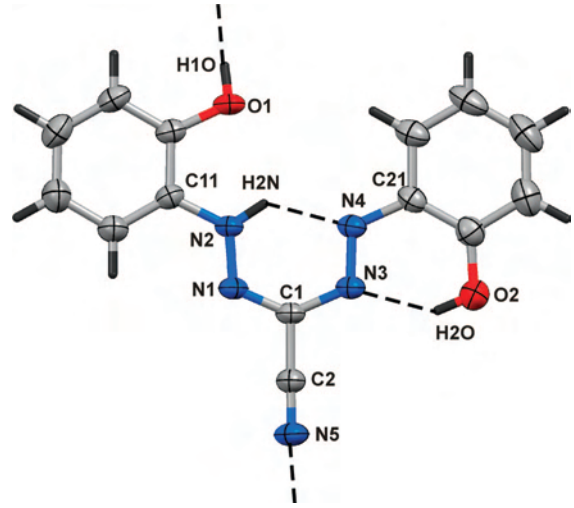

Figure 3. Molecular structure of **5e**. Thermal ellipsoids shown at 50% probability level.

The crystal structure of bis(mesityl)-3-nitroformazan **6d** is presented in Figure 4. This compound exists as the closed isomer in the solid state, as was found for the previously structurally characterized bis(2,6-dimethylphenyl) nitroformazan **6c**.[13] As is the case for the other closed derivatives, the formazan backbone in **6d** is highly delocalized, showing minimal bond-length alternation (N1−N2 1.299(2), N4−N3 1.282(2), N1−C1 1.322(2), N3−C1 1.357(2)Å). The nitro group is twisted by 14.7° relative to the plane of the formazan, while the mesityl substituents have significant torsion angles (47.2° for the Mes group attached to N2 and 26.8° for the N4-Mes group). The structure of **6b** (Supporting Information) has much in common with the structures of **6d** and **6c**, including the closed structure and delocalized nature of the formazan moiety (Table 2) as well as the moderate twisting of the aromatic substituents (17.27° and 3.60°) and the nitro group (23.4°) with respect to the formazan plane.

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg)

	5d	5e	5f	6b	6d
N1−N2	1.325(2)	1.3101(15)	1.292(3)	1.305(2)	1.299(2)
N3−N4	1.269(2)	1.2904(15)	1.296(3)	1.2877(19)	1.282(2)
C1−N1	1.304(2)	1.3180(18)	1.355(4)	1.320(2)	1.322(2)
C1−N3	1.392(2)	1.3798(18)	1.353(4)	1.357(2)	1.357(2)
C1−N1−N2	116.38(15)	118.13(11)	117.3(3)	117.19(15)	117.81(15)
C1−N3−N4	112.45(14)	115.11(11)	115.5(2)	114.59(15)	114.44(15)

X-ray structures of formazans **5a**−**c** and **6a**,**e**,**f** could not be obtained. In order to probe the solid-state conformation of these derivatives, solid-state electronic spectra (diffuse reflectance mode) were obtained for all of the 3-cyano- and 3-nitroformazans. The spectrum of **5d** (whose crystal structure (Figure 2) confirms it to be the open isomer) has a maximum at 453 nm with a shoulder on the low-energy side (∼530 nm; Figure 5). The *p*-tolyl and 2,6-dimethylphenyl derivatives **5b** and **5c** have spectral signatures which closely resemble those found for **5d**, suggesting that all three compounds have the same solid-state structure (the open isomer). In contrast, the reflectance spectrum of the diphenyl derivative **5a** consists of a broad maximum at 407 nm and a weak shoulder above 500 nm. The qualitative differences between the spectra of **5a** and the spectra of **5b**−**d** suggest that **5a** may adopt the linear structure in the solid state; qualitative color differences have long been employed to assess the presence of different formazan isomers in solution[1] (see below). For example, solution studies of thioether-substituted formazans (**1**, $R_3 = -SR$) have been correlated with isomer structure, and the linear ones are known to have the shortest wavelength maxima. The two cyanoformazans **5e** and **5f** have qualitatively different diffuse reflectance spectra (Supporting Information) from the other four cyanoformazans, with maxima near 500 nm and between 600 and 750 nm, consistent with their existence as closed isomers in the solid state.

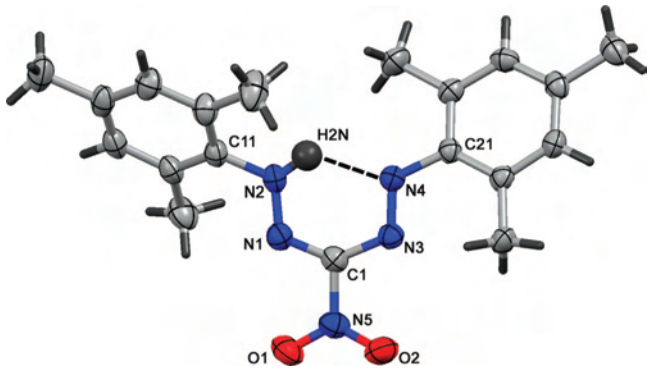

Figure 4. Molecular structure of **6d**. Thermal ellipsoids shown at 50% probability level.

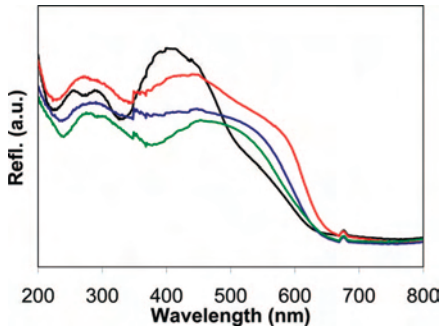

Figure 5. Diffuse reflectance spectra of **5a** (black line), **5b** (red), **5c** (blue), and **5d** (green).

Of the six nitroformazans prepared, derivatives **6b**, **6c**,[13] and **6d** have been crystallographically confirmed to be closed isomers in the solid state. These derivatives all have visible maxima between 450 and 500 nm and weaker maxima above 550 nm in their diffuse reflectance spectra; subtle variations between the maxima of these compounds may be due to substituent effects (see below). 3-Nitroformazans **6a** and **6f** also appear to be closed isomers on the basis of the similarities of their reflectance spectra to those of **6b**−**d.** The spectrum of the 2,6-diisopropyl derivative **6e** stands out from the others, as its higher-energy visible maximum is blue-shifted to 400 nm. This blue shift is probably *not* due to this formazan adopting a different isomer from the other 3-nitroformazans but rather to effects of twisting of the substituted N-phenyl rings caused by the bulky ortho substituents. Similar conformational effects of the Dipp substituents are evident in the solution UV–visible spectra (see below). The solid-state structures of related *β*-diketimines **2** with the Dipp substituent (including those with $R_2 = R_4 = H$) all show large torsion angles between the phenyl substituents and the NCCCN backbone.[20,21]

Solution Electronic Spectra and NMR Studies. The solid-state isomeric possibilities available to (and seen for) formazans (Figure 1) are also possibilities in solution.[1] The preferred conformations are, not surprisingly, substrate-dependent; some derivatives exist as a mixture of isomers in solution, and the situation is further complicated by their solvatochromism[22] and the fact that some derivatives can be photochemically interconverted.[8,17,23,24]

There have been several reports describing the synthesis and (partial) characterization of 3-cyanoformazans. Many of these derivatives adopt the closed structure as evidenced by (1) ^{1}H NMR chemical shifts of the NH proton at approximately 14–15 ppm (∼2 ppm further downfield than the corresponding NH chemical shift in *β*-diketimines **1** with 3-cyano or 3-nitro substituents),[21,25] (2) the absence of *ν*(NH) peaks in the infrared spectra (in solution and in the solid state), due to the strong intramolecular N−H···N hydrogen bonding exclusive to this isomer, and (3) UV–visible absorption maxima near and particularly above 500 nm. The

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Table 2. Ratios of Formazan Isomers in Solution for 3-Cyano- and 3-Nitroformazans

compound	solvent	closed	linear	open
5a	CD_2Cl_2	0	0.78	0.22
5b	CD_2Cl_2	0	0.85	0.15
5c	CD_2Cl_2	0	0.85	0.15
5d	CD_2Cl_2	0	0.87	0.13
5e	d_6-DMSO	1.00	0	0
5f	d_6-DMSO	0.88	0.12	0
6a	CD_2Cl_2	1.00	0	0
6b	CD_2Cl_2	1.00	0	0
6c	CD_2Cl_2	1.00	0	0
6d	CD_2Cl_2	1.00	0	0
6e	CD_2Cl_2	1.00	0	0
6f	CD_2Cl_2	1.00	0	0

closed isomers of 3-cyanoformazans can be unequivocally assigned by comparison of their various spectral features with other reported 3-cyanoformazans which are built into a macrocyclic structure (in which the formazan can *only* exist in the closed structure).[26] However, other 3-cyanoformazans have been reported which, on the basis of NMR data (principally δ(NH) ~ 10–11 ppm), must exist as either the open or the linear isomers.[27,28]

Table 2 summarizes the solution NMR data for the 3-cyano- and 3-nitroformazans. The ^{1}H NMR spectra of each of the 3-nitroformazans **6a**−**f** contain a singlet between 14.4 and 15.4 ppm corresponding to the NH proton, thereby confirming that all the nitroformazans exist in the closed structure in dichloromethane solution. In contrast, the ^{1}H NMR spectra of the 3-cyanoformazans suggest a (substrate-dependent) range of isomeric possibilities. The spectra of cyanoformazans **5a**−**d** have two distinct resonances attributable to the NH protons. The dominant resonance falls in the range 11.2–12.5 ppm, while the minor peak appears between 8.8 and 9.2 ppm. The positions of both of these sets of NH resonances rule out the closed isomer as a possibility for either the major or minor component for these four compounds, and the close correspondence of the positions of the major and minor resonances suggests that the identity of the major and minor components are the same for each **5a**−**d**. The minor component of the spectra (both ^{1}H and ^{13}C spectra; see Supporting Information for details) of **5a**−**d** clearly show the presence of inequivalent Ar groups on R_1 and R_5, whereas for the major isomer, R_1 and R_5 are equivalent. Hutton et al. have performed extensive NMR and spectroscopic studies on 1,5-diaryl-3-methylthioformazans (**1**; $R_3 = SCH_3$) which also exists in different isomeric forms.[19,24] In this series of compounds, the open structure is assigned to the symmetric set of NMR peaks; the equivalence of R_1 and R_5 arises from rapid tautomerization (Figure 6), possibly via the corresponding "closed" structure (see Figure 1). The linear structure does not tautomerize rapidly, and so the R_1 and R_5 groups appear as inequivalent substituents. On the basis of Hutton's analyses, we assign the dominant isomer in solution for **5a**−**d** to the open structure, and the minor component corresponds to the linear isomer. The 3-cyanoformazans **5e** and **5f** exist predominantly as the *closed* isomers with minor components of the open form. The NMR spectra of these two compounds were obtained in d_6-DMSO, precluding direct comparisons with the other 3-cyanofromazans—though we note that **5e** and **5f** do take on the closed structure in the solid state, and related *ortho*-functionalized 3-cyanoformazans appear to be closed in other solvents.[26]

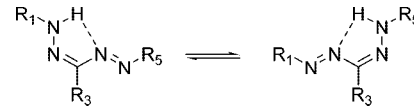

Figure 6. Tautomerism of "open" formazans.

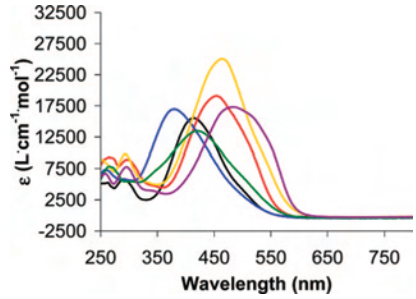

Figure 7. UV–visible spectra of **5a** (black line), **5b** (red line), **5c** (blue line), **5d** (green line), **5e** (purple line), and **5f** (orange line) in CH_2Cl_2.

Formazans are intensely colored compounds and as such have been extensively characterized using UV–visible spectroscopy.[1] A superficial correlation between formazan conformation and their color exists: Formazans that are "red" in solution are assigned the closed structure, "orange" formazans are open, and "yellow" formazans are linear. Generally, however, more sophisticated structure/spectroscopy relations have not been undertaken within a closely related subseries of formazans. The 3-cyano- and 3-nitroformazans described herein provide such an opportunity.

The solution electronic spectra of cyanoformazans **5a**−**5f** are presented in Figure 7. The low energy transitions are highly substrate-dependent, spanning a range of nearly 200 nm for these six compounds. The visible bands are believed to be charge-transfer in nature, on the basis of their extremely high extinction coefficients and solvatochromsim. Indeed, the bis(*p*-tolyl) analogue **5b** has its lowest energy absorption max at 453 nm, red-shifted by some 40 nm compared to **5a** with the less-electron-donating N-phenyl substituents. The 2,6-dimethylphenyl groups in **5c** lead to a strong blue shift (λ_{max} = 381 nm) compared to **5a** or **5b**, most likely from the ortho methyl groups favoring nonplanar orientation of the aromatic rings relative to the formazan plane. This also holds for the bis(mesityl) derivative **5d**, but the extra *p*-Me group leads to a red shift (λ_{max} = 423 nm) compared to **5c**. Compounds **5e** and **5f** exist mainly as closed isomers and are red-shifted substantially from the other 3-cyanoformazans; both have multiple absorptions above 450 nm. The 2-hydroxyphenyl derivative **5e** has the longest wavelength absorptions of all of the 3-cyanoformazans, possibly because

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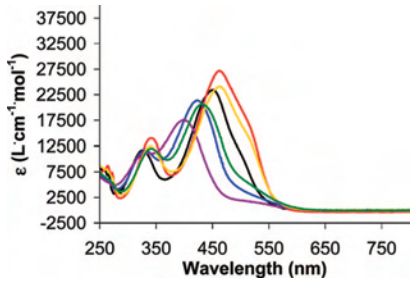

Figure 8. UV–visible spectra of **6a** (black line), **6b** (red line), **6c** (blue line), **6d** (green line), **6e** (purple line), and **6f** (orange line) in CH_2Cl_2.

the additional hydrogen bonding involving the OH groups provides further stability to the closed (coplanar) structure.

The electronic spectra of 3-nitroformazans **6a**−**f** are shown in Figure 8. All six compounds have an absorption maximum near 325–342 nm that is relatively substrate-independent. The principle visible absorption maxima fall between 398 and 464 nm; in addition, there are shoulders on the low-energy side of the main maximum. Comparisons between the various 3-nitroformazan derivatives are facilitated by the fact that they all adopt the closed structure in solution (see above). For the nitroformazans without ortho-phenyl substituents, the λ_{max} of the visible maxima increase with the electron-dontating ability of the aromatic (**6a**, 452; **5b**, 464; and **6f**, 470 nm). The two derivatives with *ortho*-methyl groups have considerably blue-shifted maxima (**6c,** 425; **6d**, 432 nm) and the 2,6-diisopropylphenyl derivative **6e** is blue-shifted even more (to 398 nm), suggesting that for these bulkier derivatives the aromatic groups are more twisted with respect to the formazan plane.

Conclusions

The reaction of "active methylene" compounds with diazonium cations represents an expeditious route to formazans with cyano or nitro groups as substituents at C3. We have used the classical (aqueous) synthesis to prepare range of 3-cyano- and 3-nitroformazans. We have also developed an alternate (nonaqueous) method which facilitates the synthesis of previously unknown formazans with bulky substituents on the nitrogen atoms. We have comprehensively characterized these compounds in solution as well as in the solid state—a necessary first step in the development of formazan chemistry, as the characterization of most formazans—the vast majority of which were prepared over a half-century ago—remains incomplete.

Conjugated, polydentate, anionic N-donor ligands are some of the most important ancillary ligand classes in inorganic chemistry. Chief among these are frameworks based on amidines,[29] aminotroponimines,[30] diiminopyridines,[31] diaazabutadienes,[32] and particularly the β-diketimines. In this context, the 3-cyano- and 3-nitroformazans described herein have the potential to be included among the more well-known ligand families. Efforts are in progress to develop the transition metal chemistry of some of these ligands.[33]

Experimental Section

General Considerations. Solvents were dried and distilled under argon prior to use. All reagents were purchased from Aldrich and used as received. Diazonium tetrafluoroborate salts were prepared according to literature procedures[14] and used immediately. Formazans **5a**,[34] **5b**,[28] **5e**,[35] and **5f**[36] and **6a**,[9] **6b**,[9] and **6c**[13] have been reported previously; however, in all cases, the characterization of these compounds was either not reported or incomplete. NMR spectra were recorded on a 300 or 500 MHz instrument. ^{1}H NMR shifts were assigned specifically with respect to each isomer present; ^{13}C NMR shifts were tabulated together, regardless of which isomers were present. 2D spectroscopy was not useful in solving this problem, as the low concentration of the less abundant isomer did not allow for high-quality spectra to be obtained. Infrared spectra were recorded as KBr pellets. UV–vis and diffuse reflectance spectra were recorded using a Cary 50 Scan instrument (1.1% in $BaSO_4$). Common features in all of the reflectance spectra at 348 and 675 nm are artifacts of the experiment and do not involve absorption by the compounds. Mass spectra were recorded on a Kratos Concept IH mass spectrometer system. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC.

X-Ray Structure Determination. X-ray diffraction data were collected on a Bruker PLATFORM/SMART 1000 CCD with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods (SHELXS-97). Complete crystallographic data for **5d**−**f**, **6b**, and **6d** have been deposited as electronic Supporting Information.

Synthesis of 3-Cyano-1,5-phenylformazan (5a). To a solution of aniline (3.72 g, 40 mmol), 12 M concentrated hydrochloric acid (10 mL), and water (10 mL) at −5 °C was added sodium nitrite (3.00 g, 43 mmol) in small portions over a 10 min period. After 15 min of stirring, the mixture was added to a second solution containing cyanoacetic acid (1.70 g, 20 mmol), sodium hydroxide (8.00 g, 200 mmol), and water (100 mL) at 0 °C over a 30 min period. The resulting solution was filtered to remove a black solid, and the organics were extracted into dichloromethane (3 × 250 mL). After removal of the solvent, the resulting dark orange solid was purified via column chromatography (neutral alumina and dichloromethane). The eluate was concentrated *in vacuo* to afford **5a** as an orange microcrystalline solid. Yield: 2.45 g, 49.1%. Mp.: 134–136 °C (dec). ^{1}H NMR (CD_2Cl_2): (*open isomer*) δ 12.47 (s, 1H, NH), 7.68 (d, 4H, $J = 7$ Hz), 7.51 (t, 4H, $J = 7$ Hz), 7.45–7.30 (m, 2H, $J = 7$ Hz); (*linear isomer*) δ 9.22 (s, 0.3H, NH), 7.95–7.85 (m, 0.5H), 7.35–7.15 (m, 0.4H). ^{13}C NMR (CD_2Cl_2): δ 152.6, 147.0, 141.5, 132.5, 130.4, 130.2, 129.9, 129.7, 126.2, 125.6, 123.6, 120.0, 116.1, 114.5 ppm. FT-IR (KBr): 3214 (m), (ν(NH)), 2226 (m) (ν(CN)), 1527 (s), 1272 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 257 nm ($\epsilon = 5250$), 291 nm ($\epsilon = 5750$), 413 nm ($\epsilon = 15500$). MS (EI): *m/z* 249 (M^+, 25%). Anal. calcd for $C_{14}H_{11}N_5$: C, 67.46; H, 4.45; N, 28.10. Found: C, 67.46; H, 4.44; N, 28.11.

General Procedure for Formazans 4b−f: 3-Cyano-1,5-p-tolylformazan (5b). To a solution of *p*-toluidine (4.30 g, 40 mmol), 12 M concentrated hydrochloric acid (10 mL), and water (10 mL)

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at −5 °C was added sodium nitrite (3.00 g, 43 mmol) in small portions over a 10 min period. After 15 min of stirring, the mixture was added to a second solution containing cyanoacetic acid (1.70 g, 20 mmol), sodium hydroxide (8.00 g, 200 mmol), and water (100 mL) at 0 °C over a 30 min period. The resulting orange solid was isolated via filtration and purified via column chromatography (neutral alumina and dichloromethane). The eluate was concentrated *in vacuo* to afford **5b** as a dark orange solid. Yield: 2.70 g, 48.7%. Mp.: 198–200 °C (dec). ^{1}H NMR (CD_2Cl_2): (*open isomer*) δ 12.60 (s, 1H, NH), 7.58 (d, 4H, $J = 7$ Hz), 7.22 (d, 4H, $J = 7$ Hz), 2.32 (s, 6H); (*linear isomer*) δ 9.04 (s, 0.2H, NH), 7.69 (s, 0.5H), 2.35 (s, 0.8H), 2.28 (s, 0.9H). ^{13}C NMR (CD_2Cl_2): δ 150.8, 145.0, 143.5, 140.4, 139.3, 135.5, 130.9, 130.8, 130.6, 130.4, 130.4, 125.8, 123.5, 119.9, 115.9, 114.9, 21.9, 21.6, 21.2 ppm. FT-IR (KBr): 3220 (ν(NH)), 2224 (ν(CN)), 1530, 1264 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 265 nm ($\epsilon = 9250$), 299 nm ($\epsilon = 9500$), 453 nm ($\epsilon = 19000$). MS (EI): *m*/*z* 277 (M^+, 35%). Anal. calcd for $C_{16}H_{15}N_5$: C, 69.29; H, 5.45; N, 25.25. Found: C, 69.31; H, 5.40; N, 24.25.

3-Cyano-1,5-(2,6-dimethylphenyl)formazan (5c). Yield: 81.9%. Mp.: 118–120 °C. ^{1}H NMR (CD_2Cl_2): (*open isomer*) δ 11.41 (s, 1H, NH), 7.18 (s, 6H), 2.48 (s, 12H), 2.33 (s, 6H); (*linear isomer*) δ 8.87 (s, 0.2H, NH), 7.15 (s, 0.9H), 2.45 (s, 1H), 2.43 (s, 1H). ^{13}C NMR (CD_2Cl_2): δ 150.1, 144.0, 138.1, 133.0, 132.6, 131.7, 131.3, 130.3, 130.1, 129.9, 129.2, 127.9, 127.4, 125.4, 124.8, 122.5, 118.5, 114, 108.3 ppm. FT-IR (KBr): 3313 (ν(NH)), 2219 (m) (νCN), 1525 (s), 1281 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 260 nm ($\epsilon = 7500$), 381 nm ($\epsilon = 17\,000$). MS (EI): *m*/*z* 305 (M^+, 20%). Anal. calcd for $C_{18}H_{19}N_5$: C, 70.80; H, 6.27; N, 22.93. Found: C, 70.53; H, 6.19; N, 22.47.

3-Cyano-1,5-mesitylformazan (5d). Yield: 60.1%. X-Ray quality crystals were grown by slow evaporation of a dichloromethane solution in a NMR tube. Mp.: 180–182 °C. ^{1}H NMR (CD_2Cl_2): (*open isomer*) δ 11.21 (s, 1H, NH), 6.99 (s, 4H), 2.45 (s, 12H), 2.33 (s, 6H); (*linear isomer*) δ 8.75 (s, 0.2H, NH), 6.94 (s, 0.5H), 2.43 (s, 1H), 2.39 (s, 1H). ^{13}C NMR (CD_2Cl_2): δ 147.7, 141.8, 140.8, 139.7, 133.6, 132.9, 130.9, 130.8, 130.4, 127.4, 114.2, 21.5,21.4, 21.2, 20.2, 18.8 ppm. FT-IR (KBr): 3314 (ν(NH)), 2224 (m) (ν(CN)), 1524 (s), 1273 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 265 nm ($\epsilon = 7500$), 423 nm ($\epsilon = 13\,500$). MS (EI): *m*/*z* 333 (M^+, 25%). Anal. calcd for $C_{20}H_{23}N_5$: C, 72.04; H, 6.95; N, 21.00. Found: C, 71.90; H, 7.05; N, 21.08.

3-Cyano-1,5-dihydroxyphenylformazan (5e). 5e was purified via column chromatography (silica gel and ethyl acetate). Yield: 77.0%. X-ray-quality crystals were grown via slow evaporation of a toluene/hexanes solution in glass tubes (5 mm diameter). Mp.: 182–184 °C. ^{1}H NMR (d_6-DMSO): δ 13.12 (s, 1H, NH), 10.45 (s, 2H, OH), 7.61 (d of d, 2H, $J = 8$ Hz, 2 Hz), 7.24 (t of d, 2H, $J = 8$ Hz, 2 Hz), 7.02 (d, 2H, 8 Hz), 6.94 (t, 2H, 8 Hz) ppm. ^{13}C NMR (d_6-DMSO): δ 151.0, 134.3, 130.3, 125.0, 120.1, 117.2, 117.1, 115.2 ppm. FT-IR (KBr): 3309 (m, br, OH), 2240 (m) (CN), 1611 (m), 1512 (s), 1475 (s), 1230 (s), 742 (s) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 258 nm ($\epsilon = 6750$), 296 nm ($\epsilon = 7750$), 484 nm ($\epsilon = 17\,250$). Anal. calcd for $C_{14}H_{18}N_5O_2$: C, 59.78; H, 3.94; N, 24.90. MS (EI): *m*/*z* 281 (M^+, 40%). Found: C, 59.74; H, 4.11; N, 24.55.

3-Cyano-1,5-dimethoxyphenylformazan (5f). Yield: 66.6%. X-ray-quality crystals were grown via slow evaporation of a dichloromethane solution in glass tubes (5 mm diameter). Mp.: 140–142 °C. ^{1}H NMR (d_6-DMSO): (*closed isomer*) δ 13.68 (s, 1H, NH), 7.68 (d of d, 2H, $J = 8$ Hz, 1 Hz), 7.43 (t of d, 2H, $J = 8$ Hz, 2 Hz), 7.24 (d, 2H, 8 Hz), 7.07 (t, 2H, $J = 8$ Hz), 3.97 (s, 6H) ppm; (*open isomer*) δ 10.24 (s, 0.1 H, NH), 7.53 (d, 0.4H, 8 Hz), 3.95 (s, 1H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.4, 135.3, 131.1, 130.7, 125.0, 121.2, 116.2, 115.6, 112.8, 56.3, 56.1 ppm. FT-IR (KBr): 2224 (m) (CN), 1506 (s), 1485 (s) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 250 nm ($\epsilon = 9000$), 293 nm ($\epsilon = 9750$), 464 nm ($\epsilon = 25\,000$). MS (EI): *m*/*z* 309 (M^+, 70%). Anal. calcd for $C_{16}H_{15}N_5O_2$: C, 62.13; H, 4.89; N, 22.64. Found: C, 62.28 H, 4.86; N, 22.32.

Method (b). Sodium hydride (0.50 g, 20 mmol) was added to a blood-red solution of **5e** (1.405 g, 5 mmol) in dry tetrahydrofuran (200 mL) at −78 °C. The mixture was allowed to warm slowly to room temperature with stirring under argon overnight, resulting in a purple solution. The mixture was once again cooled to −78 °C and treated with methyl iodide (17.1 g, 7.5 mL, 120 mmol) before it was allowed to warm slowly to room temperature with stirring under argon overnight, resulting in a dark violet solution. The solvent was removed in vacuo, yielding a dark violet solid. Treatment with water (150 mL) at room temperature for 2 h produced a red solid. The solid was filtered, before being rinsed with water and pentane. Recrystallization from a saturated methanolic solution afforded **5f** as a microcrystalline red solid, yield: 1.42 g, 91%.

General Procedure for Formazans 6a,b: 3-nitro-1,5-phenylformazan (6a). To a solution of aniline (8.61 g, 92 mmol), 12 M concentrated hydrochloric acid (25 mL), and water (50 mL) at 0 °C was added sodium nitrite (7.52 g, 109 mmol) in small portions over a 10 min period. After 30 min of stirring, the mixture was added to a second solution containing nitromethane (2.82 g, 46 mmol), sodium hydroxide (8.00 g, 100 mmol), and water (100 mL) at 0 °C over a 60 min period. The resulting solution was filtered, and the solid was triturated with methanol. The solid was then purified via recrystallization from a hot methanolic solution affording **6a** as a poppy red microcrystalline solid, yield: 6.20 g, 50.1%. It should be noted that rapid addition of the diazonium salt to the nitromethane solution results in the production of a brown oil. Purification of **6a** was complicated by the presence of this oil, and repeated crystallizations were often necessary to obtain pure samples of **6a**, decreasing the isolated yield. Mp.: 138–140 °C. ^{1}H NMR (CD_2Cl_2): δ 15.16 (s, 1H, NH), 7.66 (d, 4H, $J = 8$ Hz), 7.45 (t, 4H, $J = 7$ Hz), 7.35 (t, 2H, $J = 7$ Hz). ^{13}C NMR (CD_2Cl_2): δ 146.8, 146.1, 130.6, 130.4, 120.4 ppm. FT-IR (KBr): 1551 (s), 1354 (s), 1281 (s), 754 (s) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 325 nm ($\epsilon = 11\,500$), 452 nm ($\epsilon = 23\,750$). MS (EI): *m*/*z* 269 (M^+, 25%). Anal. calcd for $C_{13}H_{11}N_5O_2$: C, 57.99; H, 4.12; N, 26.01. Found: C, 58.02; H, 3.85; N, 26.16.

3-Nitro-1,5-p-tolylformazan (6b). Yield: 47.5%. It should be noted that rapid addition of the diazonium salt to the nitromethane solution results in the production of a brown oil. Purification of **6b** was complicated by the presence of this oil, and repeated crystallizations were often necessary to obtain pure samples of **6b**, decreasing the isolated yield. X-ray-quality crystals were grown via slow cooling of a saturated methanolic solution of **6b**. Mp.: 124–126 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 15.34 (s, 1H, NH), 7.64 (d, 4H, $J = 8$ Hz), 7.33 (d, 4H, $J = 8$ Hz), 2.43 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 146.1, 144.7, 141.4, 131.0, 120.3, 21.7 ppm. FT-IR (KBr): 1547 (s), 1351 (m), 1282 (s), 816 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 265 nm ($\epsilon = 8250$), 340 nm ($\epsilon = 14\,000$), 464 nm ($\epsilon = 27\,500$). MS (EI): *m*/*z* 297 (M^+, 15%). Anal. calcd for $C_{15}H_{15}N_5O_2$: C, 60.60; H, 5.09; N, 23.56. Found: C, 60.61; H, 5.06; N, 23.43.

General Procedure for Formazans 6c−f: Synthesis of 1,5-(2,6-dimethylphenyl)-3-nitroformazan (6c). These reactions were performed under an atmosphere of dry argon. To a solution of nitromethane (1.4 mL, 26 mmol) in tetrahydrofuran (25 mL) at −78 °C was added 1.6 M *n*-BuLi in hexanes (9.6 mL, 15 mmol) over a 5 min period. The resulting slurry was allowed to stir at −78 °C for 1 h before a slurry of 2,6-dimethylphenyldiazonium

tetrafluoroborate[14] (2.82 g, 13 mmol) in tetrahydrofuran (100 mL) was added, causing the appearance of a red color. The cold bath was then removed, and the mixture was left to stir overnight, slowly darkening to a blood red color as it warmed. The mixture was filtered, concentrated, and purified via flash chromatography (alumina, dichloromethane). The dark solid was then recrystallized from a saturated methanolic solution to afford **6c** as large red needles, yield: 1.17 g (55.2%). Mp.: 122–124 °C. ^{1}H NMR (CD_2Cl_2): δ 14.51 (s, 1H, NH), 7.26–7.14 (m, 6H), 2.48 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 146.3, 144.1, 132.4, 130.4, 129.6, 20.1 ppm. FT-IR (KBr): 1544 (s), 1474 (m), 1356 (m), 1334 (m), 778 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 330 nm (ϵ = 11 750), 425 nm (ϵ = 21 250). MS (EI): *m*/*z* 325 (M^+, 10%). Anal. calcd for $C_{17}H_{19}N_5O_2$: C, 62.75; H, 5.89; N, 21.52. Found: C, 62.74; H, 5.86; N, 21.72.

1,5-Mesityl-3-nitroformazan (6d). Yield: 60.0%. Mp.: 136–138 °C. ^{1}H NMR (CD_2Cl_2): δ 14.42 (s, 1H, NH), 7.00 (s, 4H), 2.44 (s, 12H), 2.34 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 146.4, 142.2, 140.1, 132.6, 131.1, 21.4, 20.2 ppm. FT-IR (KBr): 1607 (m), 1533 (s), 1354 (m), 1334 (m), 1271 (m), 845 (m), 744 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 342 nm (ϵ = 12 000), 432 nm (ϵ = 20 750). MS (EI): *m*/*z* 353 (M^+, 10%). Anal. calcd for $C_{19}H_{23}N_5O_2$: C, 64.57; H, 6.56; N, 19.82. Found: C, 64.10; H, 6.53; N, 19.84.

1,5-(2,6-Di-*iso*-propylphenyl)-3-nitroformazan (6e). Yield 49.1%. Mp. 96–98 °C. ^{1}H NMR (CD_2Cl_2): δ 14.53 (s, 1H, NH), 7.35–7.18 (m, 6H), 3.07 (septet, 4H, J = 7 Hz), 1.15 (d, 24H, J = 7 Hz). ^{13}C NMR (CD_2Cl_2): δ 146.9, 142.9, 142.7, 130.1, 124.7, 29.2, 24.1 ppm. FT-IR (KBr): 2962 (s), 1547 (s), 1503 (m), 1470 (m), 1327 (m), 1283 (m), 746 (m) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 334 nm (ϵ = 11000), 398 nm (ϵ = 17500), 532 nm (ϵ = 1250). MS (EI): *m*/*z* 437 (M^+, 5%). Anal. Calcd for $C_{25}H_{35}N_5O_2$: C, 68.62; H, 8.06; N, 16.00. Found C, 67.83; H, 8.21; N, 15.84.

1,5-(3,5-Di-*tert*-butylphenyl)-3-nitroformazan (6f). Yield: 17.2%. Mp.: 178–180 °C. ^{1}H NMR (CD_2Cl_2): δ 15.43 (s, 1H, NH), 7.48 (d, 4H, J = 2 Hz), 7.44 (t, 2H, J = 2 Hz), 1.30 (s, 36H). ^{13}C NMR (CD_2Cl_2): δ 153.5, 146.6, 146.4, 125.2, 114.8, 35.6, 31.6 ppm. FT-IR (KBr): 2967 (s), 1604 (w), 1544 (s), 1363 (m), 1355 (m), 1299 (m), 1280 (m), 878 (w), 800 (w), 695 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 340 nm (ϵ = 12 250), 432 nm (ϵ = 24 000). MS (EI): *m*/*z* 493 (M^+, 15%). Anal. calcd for $C_{29}H_{43}N_5O_2$: C, 70.55; H, 8.78; N, 14.19. Found: C, 70.42; H, 8.88; N, 13.69.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, crystallographic data, diffuse reflectance data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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