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Electrophilicity of Cu-bound Nitriles: Toward a Method for [2+2+2] Cyclizations

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Electrophilicity of Cu-bound Nitriles:

Toward a Method for [2+2+2] Cyclizations

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This thesis for honors recognition has been approved for the Department of Chemistry.

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Abstract:

Copper nitrile systems were explored to determine the change in nitrile nucleophilicity upon coordination to copper. Both Cu(I) and Cu(II) were explored. Complexes bearing electron-withdrawing nitriles and electron-donating nitriles were analyzed using FTIR spectroscopy. The findings that Cu(I) is more reactive than Cu(II) and that an electron-withdrawing functional group on the nitrile allows better coordination are being applied to determine conditions suitable for nitrile cyclotrimerization to generate triazines. Such a synthesis could provide a cheap and sustainable alternative transition metal for promoting cyclotrimerization reactions than is currently available.

Another pathway to form a copper-bound intermediate to ultimately produce triazines is under investigation. A (Z)-4-(phenylamino)pent-3-en-2-one was formed from acetylacetone and aniline. This was subsequently reacted with copper to produce a copper-bound product.
**Introduction**

As the repercussions of environmentally harmful products are being realized, chemists are constantly striving to improve methodology to use less impactful materials, produce the least amount of byproduct possible, and find a pathway that requires the least amount of energy. One of the most effective methods to improve pathways is to employ catalysts in reactions.¹ Catalysts have both the ability to lower the activation energy that is required for the reaction to occur and to lower the amount of reagents that are used.

Currently, the metals used in the [2+2+2] cyclotrimerization of nitriles into triazines are rhodium, iridium, nickel, ruthenium, palladium, and titanium.² Several of these are platinum group metals and are rare and therefore very expensive. Ruthenium, rhodium, and palladium are known carcinogens.³ Nickel is highly inaccessible due to the earth’s molten core surrounding most deposits of nickel, and titanium can deposit dark-colored dust in lungs.³ These catalytic metals are either harmful to the environment, pose health problems, are rare or difficult to extract, or a combination of all four.

Only water soluble copper that is a byproduct of agriculture poses environmental dangers.³ Exposure to high amounts of copper over a long period of time can be deleterious to liver and kidneys.³ However, copper is a naturally occurring substance in the environment.³ It is comparatively inexpensive due to its relative abundance. Copper is a trace element that is essential in the human diet. When copper is released into the environment it becomes bound to soil or water sediment and poses no threat to drinking water.³ Relatively, copper is cheaper, more abundant, and safer for the environment and humans than the current catalysts used in the [2+2+2] cycloaddition reaction. It has the potential to greatly reduce the environmental footprint left by transition metal catalysis.
Copper is used less often than platinum group metals. The valence electron configuration for copper is $[\text{Ar}]^1d^{10}$ where the electrons fill the $3d$ orbital before the $4s$ orbital. A full $d$ subshell is a particularly stable electron configuration. Copper is thus much less willing to react than the platinum group metals, whose valence electron configurations are significantly less stable than that of copper. The reactivity of copper will be explored in the cyclotrimerization reaction.

Background

Triazines are heterocyclic molecules containing three nitrogens. The triazine can remain unsubstituted (Figure 1). In the unsubstituted form, triazines have three possible conformations in which the heteroatoms are distributed differently.

![Figure 1: Unsubstituted triazines.](image)

Triazines can also contain functional groups bound through the carbon atoms of the triazine (Figure 2). The functional groups on the triazines can vary greatly, as the aromaticity of the triazine gives stability that can support a variety of substituents. The substituted nitrile in Figure 2 is an example of an s-triazine, where the nitrogen atoms are arranged in a 1,3,5-pattern in the ring. This conformation allows for the largest substituents to be attached to the triazine: steric hindrance can be minimized between substituents when the carbon atoms that they are attached to are spaced as far apart as possible.
Figure 2: Substituted triazine where R represents a functional group.

In a cyclotrimerization, one nitrile species is used as a reagent. Through catalysis, the nitrile forms a heterocycle (Figure 3). Because the heterocycle is formed from three molecules of the same nitrile, the resulting functional groups on the triazine will be equivalent. Many functional groups can be supported by triazines. Cyclotrimerizations of nitriles use minimal reagent and are widely applicable. A [2+2+2] cycloaddition reaction is one of the most important reactions that occurs with the formation of several bonds simultaneously.

Figure 3: Cycloaddition formation with functional group represented by R.

S-triazines have been used in herbicides since the 1950’s, namely the herbicide Atrizine (Figure 4). Herbicides containing compounds of the triazine family are used in the production of sorghum, sugarcane, pineapple, soybeans, potatoes, and tomatoes to combat perennial weed growth alongside the crops; the most notable usage of a triazine herbicide occurred when Atrizine revolutionized the maize industry by finally allowing the control of broadleaf weeds.
Triazines are also commonly known for their usage in the explosive industry. RDX, TNT, and HMX are the most common explosives that contain a triazine (Figure 5). These explosives are classified as unstable and are known to explode upon initiation by a sudden shock or high temperature, and are thus highly effective for their desired usage.

The third major application of triazines is in the pharmaceutical industry. Triazines are used to control postoperative vomiting and motion sickness. Triazine-based pharmaceuticals are also used for the prevention and treatment of nausea and dizziness and are additionally used in the management of diseases that affect the vestibular apparatus. Cyclizine hydrochloride is a triazine-based drug that is known to possess anesthetic properties.

Figure 4: Structure of the triazine molecule found in Atrazine: 1-chloro-3,5-diisopropylamino-2,4,6-triazine.

Figure 5: Structures of triazine-containing TNT, RDX, and HMX.
years there has been continuing interest in triazines as a possible combatant against cancer. 
Triamino-substituted 1,3,5-triazines possess antitumor activity depending on the substituent 
group on the triazine.\(^9\) Triazines are being explored further to determine what role they could 
potentially assume in the fight against cancer.

Because of the applications of triazines in the major fields of pharmaceuticals, 
explosives, and herbicides, an optimization of the pathway to form triazines could have the 
potential to financially benefit a number of industries as well as reduce the harm that the 
current metal catalysts have on the environment.

*Copper complexes with nitriles as intermediates*

Nitriles can undergo [2+2+2] cyclotrimerization reactions to form triazines. Transition 
metal complexes are often intermediates for the cyclotrimerization in which the transition metal 
acts as a catalyst.\(^10\) Nitriles can react with metals in terminal \(\sigma\)-bonds (Figure 6). It is commonly 
known that copper binds in an octahedral geometry pattern or tetrahedral geometry pattern.

![Figure 6: Nitriles form terminal \(\sigma\)-bonds with metals: octahedral and tetrahedral geometry, respectively.](image)

The lone pair of electrons belonging to the nitrile acts as a Lewis base upon coordination 
to the metal. Bonding in metal-CN complexes requires a \(\sigma\) donation by the Highest Occupied 
Molecular Orbital and \(\pi\) acceptance by the Lowest Unoccupied Molecular Orbital.\(^8\) Weak \(\sigma\) 
donor and \(\pi\) acceptor ability of nitriles allows the formations of organometallic complexes.\(^10\)
The resulting organometallic complexes can subsequently be used in reactions such as insertions, couplings, and nucleophilic or electrophilic attack\textsuperscript{10}, of which nucleophilic attack will be explored.

Transition metals act as Lewis acids accepting electron density from the nitrile ligands. This electron density is shifted towards the metal atom upon binding. Nitrile coordination to an electron-withdrawing metal results in the nitrile carbon being electron-poor. An electron-poor nitrile is more susceptible to nucleophilic attack due to greater electrophilicity (Figure 7).\textsuperscript{10}

\[ \text{Electron WD} \quad \overset{\equiv}{\text{C}} \quad \overset{\equiv}{\text{N}} \quad \overset{\equiv}{\text{Cu}} \]

**Figure 7**: Electron density is shifted away from the carbon due to an electron with-drawing functional group on the left and the copper metal on the right: the carbon is electrophilic.

In the present study, it is hypothesized that this would allow another nitrile to perform nucleophilic attack under certain conditions to produce the desired triazine product. Functional groups with different electron-donating and electron-withdrawing properties will be explored. Electron-withdrawing substituents pull electron density away from the nitrile, while electron-donating substituents shift electron density towards the nitrile. Coordinating a variety of nitriles to Cu(I) and Cu(II) will determine optimal reactants for cyclotrimerization.

Both Cu(I) and Cu(II) are examined to determine which species is a better catalyst to form triazines. Cu(I) catalysts exhibit higher reactivity than Cu(II) catalysts in the synthesis of hydrolytic amides.\textsuperscript{11} Cu(I) also promotes the transformation of unactivated nitriles and amines into amidines.\textsuperscript{12} Coordination with Cu(I) activates the nitriles towards nucleophilic attack.\textsuperscript{12} Cu(I) catalysts synthesize carboxylic acids from terminal alkynes in good yield under ambient...
It is possible that there is less steric hindrance with the tetrahedral molecular geometry of Cu(I) complexes than the octahedral molecular geometry of Cu(II) complexes (Figure 6).

It is predicted that Cu(I) will be more reactive in forming Cu-nitrile complexes that are susceptible to nucleophilic attack. Electron poor species are good Lewis acids, so the electron-withdrawing property of copper will be expected to make the nitrile carbon more electropositive and susceptible to nucleophilic attack. The Cu(I) species is actually less electron-poor than Cu(II), so both species must be investigated. Before cycloadditions can be performed, copper-nitrile complexes will be investigated for clues to the nucleophilic character of the coordinated nitriles (Figure 8).

Different substituents on the nitrile species will be investigated. A series of substituted nitriles with Cu(I) and Cu(II) will each be explored. These substituents vary the electron-donating and electron-withdrawing ability of the substituents. This may provide insight into optimal substituents to withdraw electron density from the nitrile carbon. All substituents will be attached para to an aromatic group on the nitrile to minimize steric hindrance. Electron-withdrawing substituents are hypothesized to cause increased reactivity of the nitrile carbon.

Coordination of a nitrile to a metal would alter the properties of the nitrile. Free nitriles have a characteristic peak when they are analyzed using IR spectroscopy. A sharp peak in the range of 2210-2260 cm\(^{-1}\) is indicative of a free nitrile. The nitrile peak in the IR would
subsequently be shifted after metal coordination. IR spectroscopy of the free and coordinated nitriles will be analyzed to determine if a change in the dipole moment has occurred, which can be indicative of altered reactivity (Figure 9).

Figure 9 shows an example of the shift of the nitrile peak. The signal in blue at 2209 cm\(^{-1}\) is assigned as the CN stretching frequency of uncoordinated 4-(dimethylamino)benzonitrile. This signal positively shifts to 2224 cm\(^{-1}\) upon coordination to Cu(I), and coordination of the nitrile to Cu(II) had a positively shifted peak at 2249 cm\(^{-1}\).

![Infrared Spectrum](image)

**Figure 9: Infrared Spectrum**

The positive $\Delta \nu$ (cm\(^{-1}\)) implies an increase in electron density around the nitrile, which is the opposite of the intended goal of making the nitrile carbon as electron-poor as possible. A negative $\Delta \nu$ would imply increased polarization of the CN bond toward the metal which could increase susceptibility to nucleophilic attack at the carbon atom. Therefore, nitriles with
negative $\Delta \nu$ will be sought. This analysis was performed on a series of nitrile species, each of which was reacted with Cu(I) and Cu(II) ions.

**Experimental**

Reagent quantities were determined using Equation 1

$$CuCl_2 + 2NaBF_4 + 6(Nitrile) \rightarrow 2NaCl + [CuNitrile_6]^{2+}[BF_4]^-$$  \hspace{1cm} (1)

with the expectation that six nitriles would coordinate to the copper (II) species using octahedral geometry, as previously discussed.

The reagent quantities in the Cu(I) series of nitriles were determined using Equation 2

$$CuCl + NaBF_4 + 4(Nitrile) \rightarrow NaCl + [CuNitrile_4]^{+}[BF_4]^-$$  \hspace{1cm} (2)

where four nitriles would be expected to coordinate with copper (I) species through tetrahedral geometry.

Reactions were performed under dry nitrogen of 99.99% purity. All reagents were purchased and used as received unless otherwise noted. Cupric chloride and cuprous chloride were dried under heat vacuum prior to use for at least two days. The anion used was NaBF$_4$ which was also dried under heat vacuum prior to use for at least two days. The copper chloride species and anion were stored in the heat vacuum between experiments to assure anhydrous conditions.

The nitriles used were acetonitrile, benzonitrile, propionitrile, 4-(methylthio)benzonitrile, 4-(methoxy)benzonitrile, 4-(trifluoromethyl)benzonitrile, 4-nitrobenzonitrile, 4-(dimethylamino)benzonitrile. All functional groups were kept at the para
position as a constant. All liquid nitriles were dried for one week prior to experimentation with molecular sieves activated in an oven on low temperature overnight.

Analysis of all products was performed using a ThermoScientific Nicolet iS10 FTIR Spectrometer with an ATR attachment. Each analysis was set to 16 scans and a resolution of 1. Nitrogen gas was blown on to the surface of the ATR and during analysis.

General Procedure for Preparation of Metal Nitriles

CuCl$_2$ and NaBF$_4$ were analytically weighed and added to a round bottom flask with magnetic stir-bar. The flask was connected to: the Schlenk line, a glass frit separator with receiving flask, and septum. The system was flushed with nitrogen for 10 minutes. The nitrile that had been dissolved into 10 mL of methylene chloride was injected through the septum (1 mol CuCl$_2$: 2 mol NaBF$_4$: 6 mol nitrile). Medium stirring and heat at 50°C were maintained for 45 minutes. The solvent was vacuumed off, leaving precipitate in the flask. Precipitate was weighed then analyzed using IR spectroscopy under gaseous flow of nitrogen. Pure nitrile, copper species, and anion were also analyzed using IR to determine where, if any, unreacted reagents had a peak. The shift of the pure nitrile to the coordinated nitrile was measured.

The same procedure and nitrile system was used with the Cu(I) species (CuCl) in a 1 mol CuCl$_2$: 2 mol NaBF$_4$: 4 mol nitrile mole ratio.

Results and Discussion

Acetonitrile was complexed with copper (II) and analyzed using FTIR spectroscopy. The acetonitrile-copper (II) complex was air sensitive and required inert nitrous conditions to avoid decomposition during the FTIR analysis. No other nitrile-copper complex exhibited air-sensitivity. It is possible that this difference between acetonitrile and the other nitriles in the
series is due to the lack of a benzene ring on acetonitrile that was present in all other nitriles. The lack of the aromatic ring, which is known for its stability, was thought to be the cause of the sensitivity experienced by the acetonitrile-copper(II) complex. Although there was a nitrile shift evident in the interferogram of the acetonitrile-copper (II) complex, the shift was in the positive $\Delta\nu$ direction which is indicative of increased electron density. Because of the unstableness and undesirable shift of electron density, acetonitrile was excluded from the copper (I) series.

**Figure 10:** The structures of the series of nitriles that was analyzed: 1. benzonitrile 2. propionitrile 3. 4-(methylthio)-benzonitrile. 4. 4-(methylxy)benzonitrile 5. 4-(dimethylamino)benzonitrile 6. 4-(trifluoromethyl)benzonitrile 7. 4-nitrobenzonitrile
Benzonitrile, propionitrile, 4-(methylthio)benzonitrile, 4-(methoxy)benzonitrile, and 4-(dimethylamino)benzonitrile all experienced a positive $\Delta \nu$ shift upon coordination to copper (II). The lack of a substituent on benzonitrile, the hydrocarbon chain of propionitrile, the methylthio group, the methoxy group, and the dimethylamino group are all substituents that are known to possess electron-donating property (Figure 10). It was not surprising that the positive shift of the nitrile peak on the interferogram was observed for each of these nitriles. An increase in wavenumber can be related to an increase in energy that will be required to vibrationally excite that bond. The increase in energy implies that their electron density has shifted towards the nitrile bond. This is the opposite of the desired effect: an increase in electron density decreases the availability for nucleophilic attack at the carbon atom.

Upon coordinating to copper(II), 4-(trifluoromethyl)benzonitrile experienced a negative shift indicative of decreased electron density around the nitrile carbon. This shift was hypothesized to occur due to the electron-withdrawing properties of the trifluoromethyl substituent group. When 4-nitrobenzonitrile, the other nitrile tested with known electron-withdrawing properties, was reacted with copper(II), the fingerprint region of the IR spectrum developed numerous new peaks that did not correspond to a shift from the free nitrile’s spectrum. These new peaks along with the disappearance of the nitrile peak altogether from the complex’s spectrum could indicate that the carbon of the nitrile complexed with the copper(II). The nitrile species that demonstrated the best IR shift using copper(II) as a catalyst was 4-(trifluoromethyl)benzonitrile. This agreed with the hypothesis that an electron-withdrawing substituent-containing nitrile would optimize the desired intermediate.

IR spectra values for the free and complexed nitrile peaks are in Table 1. All spectra are in the appendices.
**Table 1:** The series of nitriles coordinated to Cu(II) and Cu(I): the nitrile peak wavenumbers for the free and copper-complexed nitriles.

<table>
<thead>
<tr>
<th>Nitrile</th>
<th>IR Table of Analysis</th>
<th>Copper (II)</th>
<th>Copper (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>free nC≡N (cm⁻¹)</td>
<td>Complex's Frequency (cm⁻¹)</td>
<td>Measured Shift (Δcm⁻¹)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2252.43</td>
<td>2293.90</td>
<td>41.47</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>2227.98</td>
<td>2284.39</td>
<td>56.41</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>2246.77</td>
<td>2299.55</td>
<td>52.78</td>
</tr>
<tr>
<td>4-(methylthio)benzonitrile</td>
<td>2237.46</td>
<td>2263.74</td>
<td>26.28</td>
</tr>
<tr>
<td>4-(methoxy)benzonitrile</td>
<td>2218.49</td>
<td>2258.08</td>
<td>39.59</td>
</tr>
<tr>
<td>4-(trifluoromethyl)benzonitrile</td>
<td>2235.46</td>
<td>2160.05</td>
<td>-75.41</td>
</tr>
<tr>
<td>4-nitrobenzonitrile</td>
<td>2231.69</td>
<td>coordination through carbon?</td>
<td>fingerprint region</td>
</tr>
<tr>
<td>4-(dimethylamino)benzonitrile</td>
<td>2207.18</td>
<td>2248.66</td>
<td>41.48</td>
</tr>
</tbody>
</table>

The same series of nitriles that was complexed with copper(II) was also complexed with copper(I), excluding propionitrile, acetonitrile, and 4-nitrobenzonitrile. The complexed acetonitrile was extremely air-sensitive and displayed an undesirable shift in electron density. Propionitrile also did not produce the sought-after shift in electron density. Being that propionitrile is a nitrile with only a hydrocarbon chain, it is not a realistic proxy for the nitriles with large substituents that form the triazines in industry. Optimizing the catalytic pathway for nitriles with large functional groups attached to them should be explored before other nitriles. The 4-nitrobenzonitrile was also not included in the series of nitriles with copper(I).

When complexed with copper(I), 4-(methoxy)benzonitrile and 4-(dimethylamino)benzonitrile both experienced a positive shift of the nitrile peak in the IR spectra. This was consistent with their substituents’ known electron-donating properties. The positive shifts were much smaller than the positive shifts of the same nitriles when they were complexed with copper(II). This implies that Cu(I) is indeed a better metal than Cu(II) for this
reaction; Cu(I) allowed less electron density to be shifted towards the nitrile group than Cu(II) did.

The complexes of Cu(I) with benzonitrile and 4-(methylthio)benzonitrile experienced negative nitrile peak shifts. The methylthio functional group has known electron-donating properties, so the negative removal of electron density around the nitrile’s carbon atom must be attributed to Cu(I). The aromatic ring of benzonitrile also has known electron-donating properties. Cu(I) shifts electron density away from the nitrile carbon even with mild electron-donating substituents attached to the nitrile. Cu(II) did not have this ability, so Cu(I) may provide better activation of the nitrile carbon toward nucleophilic attack.

When Cu(I) was complexed to 4-(trifluoromethyl)benzonitrile, the nitrile peak was not observed any longer. There was a distinct methyl shift in the spectrum with a novel region developing further down from the nitrile peak region (Appendix 6). Upon further investigation, a complex was formed with an extremely negative nitrile peak shift. The reaction will not form the metal-nitrile complex if the reaction stoichiometry is not strictly adhered to. This combination displayed the largest negative Δν, consistent with a shift in electron density away from the carbon of the nitrile. The combination of Cu(I) and 4-(trifluoromethyl)benzonitrile will be further explored: the intermediate will be isolated and used in the cyclotrimerization step of the reaction.

Structural Analysis

IR spectroscopy provides insight into the functional groups of a molecule, but it cannot be used to determine the overall structure of a molecule. Computational chemistry also cannot state the structure of the molecule, but it can make predictions to compare against the data. To
corroborate that the product molecules are the hypothesized structures, computational chemistry was performed.

The \textit{ab initio} B3LYP theory level was used to perform calculations. The lowest unoccupied molecular orbital (LUMO)'s energies and shapes of the frontier orbitals for uncoordinated 4-(trifluoromethyl)benzonitrile were generated: the 90\% probability volume of these orbitals is shown in Figure 12, as was the LUMO for four molecules of 4-(trifluoromethyl)benzonitrile complexed to Cu(I)- the theorized molecular bonding geometry pattern for Cu(I).

The LUMO is where the reactivity of nucleophilic attack would occur. According to the resulting images, the LUMO of the nitrile carbon is very large and close to the lobe of the nitrile nitrogen in the uncoordinated molecule. In the complexed molecule, the lobe of the nitrile carbon is much more exposed. The electron density is shifted towards the substituent trifluoromethyl group and the center copper(I) atom. The calculations of the uncoordinated and coordinated complexes demonstrate the greater susceptibility of the nitrile carbon to nucleophilic attack. The vibrational frequencies that were also found using computational chemistry agreed with the experimental vibrational frequencies. This use of B3LYP theory as a structural proxy agrees with the theorized structure of four nitriles coordinated through the nitrogen to copper(I).
Figure 11: The Lowest Unoccupied Molecular Orbitals for uncoordinated and coordinated 4-(trifluoromethyl)benzonitrile using B3LYP theory.
Conclusion

In summary, the use of copper(I) as a catalyst to cyclotrimerize nitriles into triazines is likely. Copper(I) has the ability to form stable intermediates with electron-withdrawing nitriles and mildly electron-donating nitriles. Upon coordination, there was an observable shift in the IR spectra of the nitriles, which is indicative of altered reactivity. 4-(trifluoromethyl)benzonitrile is the most likely of the series of nitriles to cyclotrimerize and will be the nitrile of focus in subsequent experiments. The next step of this exploration will be to ensure the chemical identity of the metal-nitrile intermediates with NMR before reacting them to form triazines.
Acknowledgements

First and foremost, I need to thank my advisor Dr. Colin Thomas for countless hours spent on this project as well as all of his guidance and encouragement. This advancement of scientific knowledge is a direct result of his wisdom and energy. None of this would have been achievable without his leadership. I also need to thank Dr. Gerald Shields for the infinite amount of corrections and suggestions he provided in the writing of this thesis. Each of his words shaped two years of work into a scientific document that can be shared. Dr. Jennifer Geiger and Dr. Kyle Strode must be thanked for their thoughtful readings and revisions of this thesis. Carroll College also has my gratitude for having a wonderful Department of Natural Science in which to conduct research.
Works Cited


Appendix 1: IR spectra for acetonitrile
Appendix 2: IR spectra for benzonitrile

Pure benzonitrile

2227.92

benzonitrile + Cu(II)

2226.03

2284.47
Appendix 3: IR spectra for 4-methylthiobenzonitrile
Appendix 4: IR spectra for 4-methoxybenzonitrile
Appendix 5: IR spectra for 4-dimethylaminobenzonitrile
Appendix 6: IR spectra for 4-trifluoromethylbenzonitrile
Appendix 7: IR spectra for 4-nitrobenzonitrile

Pure 4-nitrobenzonitrile

4-nitrobenzonitrile + Cu(II)

2233.58