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Cu(II) Mediated Generation and Spectroscopic Study of the Tris(4-anisyl)amine Radical Cation and Dication. Unusually Shielded Chemical Shifts in the Dication

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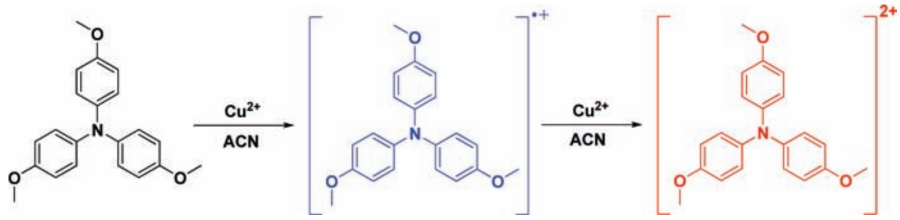
ABSTRACT



The reaction of tris(4-anisyl)amine (TAA) with Cu^{2+} ion leading to formation of the TAA radical cation and dication is described. Spectroscopic studies confirm the formation of the radical cation and dication. ^1H and ^{13}C NMR spectral studies reveal interesting structural features of the dication.

Recently we have introduced a very simple and effective method for the generation of aromatic amine radical cations.[1] The reaction involved mixing of the aromatic amines with 1 equiv of a Cu^{2+} salt such as $Cu(ClO_4)_2$ in acetonitrile (ACN) solution. In ACN, Cu^{2+} can accept an electron from aromatic amines (oxidation potential ≤1 V vs SCE), thereby leading to formation of the amine radical cation. Using triarylamines as substrates we have recently shown that the electron transfer from these amines to Cu^{2+} in ACN takes place by an outer sphere electron transfer mechanism obeying the Marcus equation.[2] Compared to other methods of amine radical cation generation (such as anodic oxidation,[3a−c] photoionization,[3d] γ-irradiation,[3e,f] and photoinduced electron transfer[3g]) where the amine radical cations are generated as transient intermediates, the present method is very simple and allows for the generation of these radical cations in a relatively stable environment in reasonably high concentrations. Taking *N*,*N*-dialkylaniline and triphenylamine derivatives as examples we have shown that this method can be effectively explored for studying the reactivity patterns of amine radical cations.[4]

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We have also shown that this method can be exploited for laboratory scale preparation of tetraalkyl and tetraphenyl benzidine derivatives.[4] In this paper we show that this simple method is capable of generating the radical cation and dication of tris(4-anisyl)amine (TAA), under reasonably stable conditions. Herein we report the results of a spectroscopic investigation of the dicationic species, including the ^{1}H and ^{13}C NMR spectroscopy, which enabled us to obtain valuable insight into the structural details of this species.

Because of the high stability and large extinction coefficient (ε) of its radical cation, TAA is a popular electron donor in photoinduced electron transfer reactions.[5] The redox potential of Cu^{2+}/Cu^{+} is at 0.952 V vs SCE in ACN.[6] Cyclic voltammogram of TAA exhibits oxidation peaks at 0.55 and 1.2 V vs SCE in ACN. Hence oxidation of TAA to its radical cation ($TAA^{\bullet+}$) by Cu^{2+} is thermodynamically feasible in ACN ($\Delta G° = -0.46$ eV), whereas oxidation to the dication (TAA^{2+}) is endergonic by 0.19 eV. Previous studies have characterized $TAA^{\bullet+}$ by its strong absorption around 720 nm.[5] The only report of the dication was by Lambert and co-workers who generated TAA^{2+} using spectroelectrochemistry in dichloromethane (DCM).[7]

The ACN solution of TAA was colorless and exhibited absorption maximum at 296 nm. Figure 1 shows the effect of adding increasing amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ to TAA (5×10^{-5} M) in ACN. When the Cu^{2+} concentration is in the range of 0−1 equiv, the absorption due to TAA decreased with a concomitant increase in absorption at 717 nm (Figure 1A). When 1 equiv of Cu^{2+} was added, absorption due to TAA disappeared completely, the intensity of 717 nm absorption was maximum, and the solution was deep blue in color. Further addition of Cu^{2+} leads to a decrease in the intensity of the 717 nm absorption with a concomitant increase in absorption at 520 nm (Figure 1B). When 2 equiv of Cu^{2+} were added, the absorption at 717 nm disappeared completely, the absorption at 520 nm was maximum, and the solution was deep red in color. Further addition of Cu^{2+} did not lead to any change in the absorption. Insets of Figure 1 show the changes in the absorbances at 717 and 520 nm as a function of [Cu^{2+}].

Based on the literature and our own studies the 717 nm absorption was assigned to $TAA^{\bullet+}$ and the 520 nm absorption was assigned to TAA^{2+} (Scheme 1).[5,7] The reaction of TAA with Cu^{2+} leading to the formation of $TAA^{\bullet+}$ was instantaneous. The formation of the dication by reaction of $TAA^{\bullet+}$ with Cu^{2+} was relatively slow and took 10−30 min for completion. Hence plots h−o in Figure 1B were recorded 30 min after mixing.

Because of the different absorption bands and change over from one band to another, the addition of 0−2 equiv of $Cu(ClO_4)_2$ to a ACN solution of TAA (5×10^{-5} M) results in a play of colors as shown in Figure 2. In fact this observation can be exploited to develop colorimetric sensors for the detection of micromolar amounts of Cu^{2+} and this work is in progress in our laboratory.

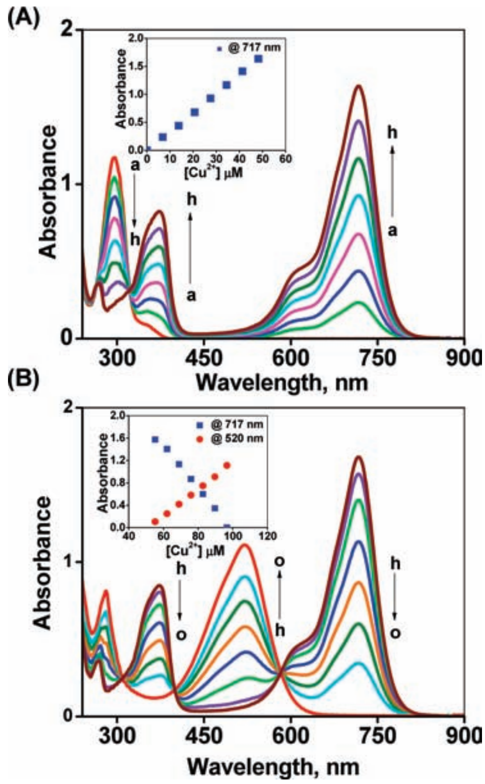
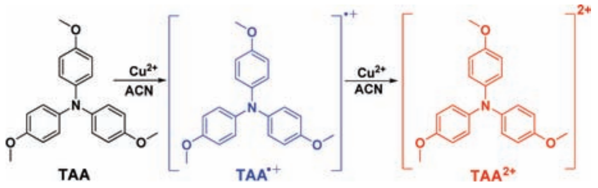


Figure 1. Effect of adding $Cu(ClO_4)_2 \cdot 6H_2O$ to TAA (5×10^{-5} M) in ACN. (A) a−h, [Cu^{2+}] varied from 0 to 1 equiv; (B) h−o, [Cu^{2+}] varied from 1 to 2 equiv. Inserts show variations of absorbances as a function of [Cu^{2+}].

Scheme 1. Reaction of TAA with Cu^{2+} in ACN



$TAA^{\bullet+}$ obtained by reaction of TAA with 1 equiv of Cu^{2+} was very stable. The solution could be kept without decomposition under ordinary laboratory conditions for several weeks. TAA could be quantitatively recovered from this solution by the addition of excess amounts of an electron donor such as triethylamine (TEA). Gould et al.[5] generated $TAA^{\bullet+}$ in ACN by spectroelectrochemistry and reported $\varepsilon = 45\,000$ M^{-1} cm^{-1}. Lambert and co-workers using the same technique reported $\varepsilon \approx 33\,000$ M^{-1} cm^{-1}

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Figure 2. Play of colors in the reaction of TAA (5×10^{-5} M) with Cu^{2+}. Cu^{2+} concentrations were 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 equiv.

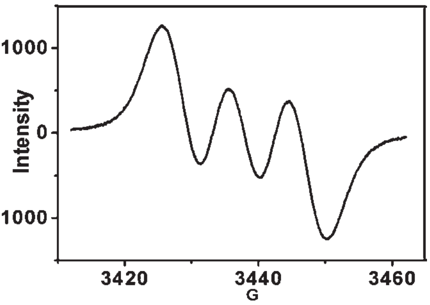

Figure 3. EPR spectrum of a solution of TAA (1×10^{-3} M) in ACN in the presence of 1 equiv of $Cu(ClO_4)_2$.

in DCM.[7] Assuming complete conversion of TAA to $TAA^{\bullet+}$, we get $\varepsilon = 32\,800\ M^{-1}\ cm^{-1}$ in ACN using data in Figure 1. Since $TAA^{\bullet+}$ is very stable and 100% recovery of TAA was possible upon addition of TEA, we believe that the ε value we report here is very accurate.

An equimolar solution of TAA and Cu^{2+} also yielded the EPR spectrum shown in Figure 3, which confirms the radical cation structure of the species generated. The three-line EPR spectrum of $TAA^{\bullet+}$ obtained is consistent with the ^{14}N triplet hyperfine interaction.[8] Attempts to record the ^1H and ^{13}C NMR spectra of $TAA^{\bullet+}$ were not successful most probably due to the presence of the unpaired electron. An IR spectrum of $TAA^{\bullet+}$ (Supporting Information, SI) shows peaks at 1637 and 1579 cm^{-1}, which indicated double bond character for C−N and C−O bonds (IR peaks in the 2300−2100 cm^{-1} region are due to CO_2, CH_3CN, and a Cu−ACN complex).

As stated previously, the formation of TAA^{2+} by reaction of $TAA^{\bullet+}$ with Cu^{2+} is endergonic. Although $\Delta G°$ is slightly positive, dication formation takes place, albeit slowly, in the presence of 1−2 equiv of Cu^{2+}, as is established from Figures 1 and 2. Lambert and co-workers reported that TAA^{2+} exhibited an absorption maximum at 532 nm ($\varepsilon \approx 20\,000\ M^{-1}\ cm^{-1}$) in DCM.[7] In ACN the absorption maximum we obtained was 520 nm ($\varepsilon = 22\,200\ M^{-1}\ cm^{-1}$). We further confirmed the assignment of the 520 nm absorption to the dicationic species by generating $TAA^{\bullet+}$ from the dicationic species upon addition of 1 equiv of neutral TAA as per eq 1 (see SI, for figure).

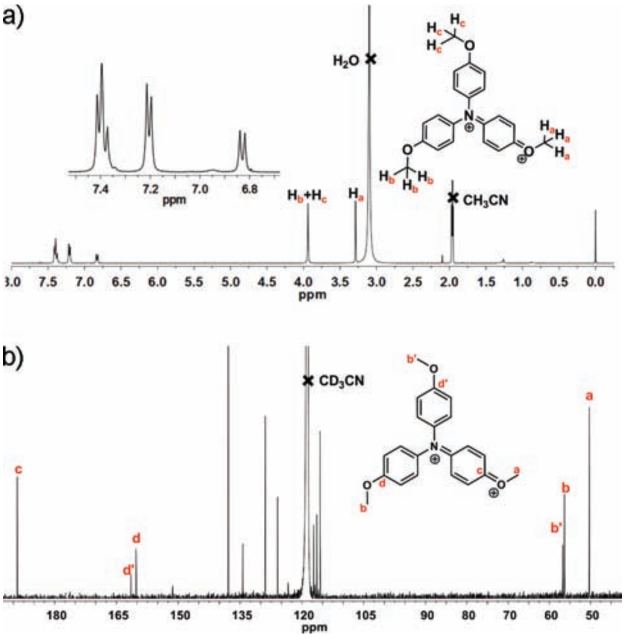

Figure 4. (a) ^1H (recorded at 263 K) and (b) ^{13}C NMR spectrum of TAA^{2+} in CD_3CN.

$$TAA^{2+} + TAA \rightarrow 2TAA^{\bullet+} \qquad (1)$$

We also observed that the 520 nm absorbing species is not EPR active indicating that it did not contain any unpaired electrons. TAA^{2+} was reasonably stable which enabled us to record its ^1H and ^{13}C NMR spectra, and these are shown in Figure 4a, b. We have compared the ^1H and ^{13}C NMR spectra (Figure 4a, b) to those of TAA (see SI) in order to derive useful information about the structure of TAA^{2+}. When compared to TAA, TAA^{2+} is highly electron-deficient and hence we would expect all the ^1H and ^{13}C peaks to shift downfield. Comparison of the spectra shows that not all peaks are down shifted. In fact some of the peaks are shifted upfield, and this cannot be explained based on electronic effects. It may be noted that Figure 4a does not show any of the ^1H NMR peaks corresponding to the parent compound TAA. The radical cation $TAA^{\bullet+}$ is NMR inactive. These two aspects essentially rule out the possibility that the NMR spectra presented in Figure 4 are due to mixtures of TAA, $TAA^{\bullet+}$, and TAA^{2+}. We expect that only the following species contribute to the NMR spectra in Figure 4a, b: (1) TAA^{2+}, (2) $[Cu(CD_3CN)_4]^+$, (3) CD_3CN, and (4) water.

TAA is a highly symmetric molecule as is evident from its ^1H and ^{13}C NMR spectra (three peaks in ^1H and five peaks in ^{13}C NMR; see SI). In the dication the methoxy carbons appear as three different peaks indicating that the symmetry is lost. The most notable feature in the NMR spectra of TAA^{2+} is the highly shielded ^1H and ^{13}C signals

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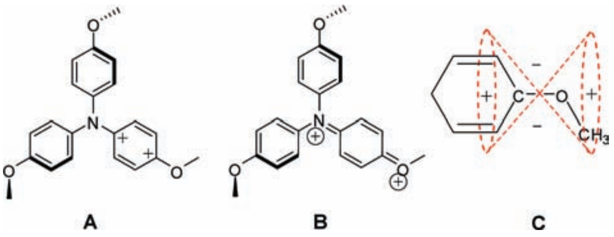
Scheme 2. Possible Structures of TAA^{2+}



of one of the methoxy groups. The other two methoxy groups exhibited a small downfield shift. In the ^{13}C NMR these methoxy groups exhibited slightly different δ values. In the ^{1}H NMR the methoxy peak corresponding to six protons was somewhat broad at 298 K (see SI) but became narrower at lower temperatures, indicating that these methoxy groups in fact have slightly different δ values. These results show that the effect of the two positive charges is confined to one of the three aryl rings and the other two, although they experience the effect of the overall positive charge of the molecule, are largely unaffected structurally. Olah and co-workers have reported ^{13}C NMR spectra of several dicationic molecules.[9,10] In light of these reports two possible structures can be considered (A and B in Scheme 2) as candidates for the structure of TAA^{2+}.

Both of these structures cannot satisfactorily explain the shielding observed for the protons and carbon of one of the methoxy groups. To explain the observed shielding it is necessary to invoke a diamagnetic anisotropy which leads to shielding of the methoxy group. Normally diamagnetic anisotropy cones of C—O and C═O have shielding regions perpendicular to the bond axes and deshielding cones along the bond axes. If we invoke the same here, the methoxy group would be in the deshielding cone which would shift the ^{1}H and ^{13}C signals downfield. Since the observed ^{1}H and ^{13}C chemical shifts are upfield we propose a reversal in the sign of the anisotropy of the diamagnetic susceptibility, which leads to shielding of atoms inside the cone (+ sign) and deshielding outside the cone (− sign), as shown in Scheme 2C. The reason for the sign reversal is not understood, but the positive charges on the molecule could be a possible reason. It may be noted that a reversal in the sign of the diamagnetic susceptibility has been reported previously for several systems.[11]

If we assume that diamagnetic anisotropy cone as shown in Scheme 2C is present in the molecule, then the observed chemical shifts are better explained by structure B (Scheme 2). Olah and co-workers reported few dicationic aromatics where the ring carbon attached to OCH_3 showed ^{13}C chemical shifts in the 170−184 ppm range.[10] They, however, did not report any shielding of the ^{1}H and ^{13}C signals of the methoxy group. If the C−O bond remains as a single bond as in the case for A (Scheme 2), shielding would shift the ^{13}C signal to < 150 ppm. On the other hand if this bond is present as C═O, which is normally observed at ∼210 ppm, then the shielding as that in C (Scheme 2) could shift the signal to the observed value of 186 ppm. Olah et al. have suggested that wherever possible, the contribution from quinoidal structures will be substantial in dicationic systems.[10] Scheme 2C shows that ring protons ortho to the methoxy group are shielded. Assignments of the protons in the ^{1}H NMR (SI) in fact show that the H_d protons in TAA^{2+} are shielded. We observed that the IR spectrum of the dicationic species exhibited a peak at 1645 cm^{-1}, (see SI) which further supported our assignment of the structure of TAA^{2+} as shown in Scheme 2B. It is to be mentioned here that the ^{1}H and ^{13}C signals in Figure 4a, b are not due to any products arising from decomposition of TAA^{2+}. In fact, more than 90% of TAA can be recovered unchanged by workup of the solutions used for recording ^{13}C NMR spectra.

In conclusion we have shown that TAA can react with 1 equiv of Cu^{2+} to generate $TAA^{\bullet+}$, whereas a reaction with 2 equiv Cu^{2+} gave TAA^{2+}, both in relatively stable conditions. $TAA^{\bullet+}$ was characterized by absorption and EPR spectra. The dicationic species was identified by its absorption spectrum, and detailed characterization of its structure was attempted based on its ^{1}H and ^{13}C NMR spectra. In order to explain the shielding observed in the ^{1}H and ^{13}C signals of one of the three methoxy groups, a reversal in the sign of the diamagnetic anisotropy cone of the C═O group is proposed.

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Supporting Information Available. General experimental procedures, photophysical measurements, and spectroscopic characterization data for TAA and its dication are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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