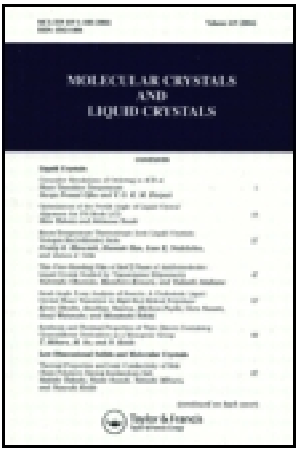

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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To cite this article: Matthew A. Kellett & David G. Whitten (1991): Electron Transfer Photofragmentation Reactions of 1,2-Diamines. Studies of the Mechanism of the Carbon-Carbon Bond Cleavage, Molecular Crystals and Liquid Crystals, 194:1, 275-280

To link to this article: http://dx.doi.org/10.1080/00268949108041176

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 275–280
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Printed in the United States of America

ELECTRON TRANSFER PHOTOFRAGMENTATION REACTIONS OF 1,2-DIAMINES. STUDIES OF THE MECHANISM OF THE CARBON-CARBON BOND CLEAVAGE

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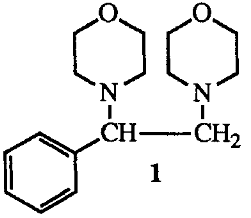
Abstract A series of 1,2-diprimary and ditertiary amines have been found to undergo chemically clean oxidative photofragmentation to yield the corresponding aldehydes, presumably via hydrolysis of the iminium ions , upon irradiation in the presence of UV or visisble light absorbing electron acceptors(thioindigo, ß-lapachone, dicyanoanthracene, or tetracyanoanthracene). The reaction is proposed to follow a mechanism analogous to that previously developed for 1,2-aminoalcohols, however, for the diamines, the fragmentation is indicated to be an unassisted process involving only the photogenerated cation radical.

Keywords: Photoinduced electron transfer fragmentation of diamines

The quenching of excited electron acceptors by electron transfer from amine donors and the further chemical reactions of these species continue to be the focus of extensive research.[1-6] Among the various reactions of the photogenerated radical ion pairs, fragmentation via C-C bond cleavage has been shown to be a prominent and often clean path for aminoalcohols and aminoketones[7-12]; past experiments have shown that the dehydrofragmentation of aminoalcohols is strongly acceptor dependent and consistent with a mechanism in which the acceptor anion radical acts as a base to promote cleavage of the donor cation radical in a reaction closely analogous to the two-electron "Grob" fragmentation.[13,14] Here we present studies of the photo-oxidative fragmentation of 1,2-diamines, a reaction which appears to be quite general and which shows both similarities and yet remarkable contrasts to the aminoalcohol cleavage.

The acceptor-dependence of aminoalcohols as compared to ditertiary amines was observed by the study of styrene derived amine donors.[15] The two compounds which were compared were the diamine **1**, 1,2-dimorpholino-1-phenyl ethane, and the analogous aminoalcohol **1A**, 1-phenyl-2-morpholinoethanol.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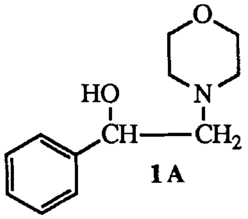

1A

Studies of the photolysis of solutions of **1** and **1A** with a variety of acceptors and in several different solvents demonstrated that the relative reactivities of the two donor substrates could be reversed by the manipulation of acceptor anion-radical basicity and by the polarity of the solvent. With acceptor molecules that have relatively basic anion radicals, such as thioindigo(TI) or ß-lapachone(ß-lap), the aminoalcohol was found to be the more reactive by a factor of as much as 2:1, due to the deprotonation assistance on the fragmentation. However, with relatively non-basic acceptors, dicyano-(DCA) and tetracyanoanthracene(TCA), the diamine was the more reactive by as much as 33:1 for TCA, due to its ability to undergo fragmentation through an unassisted manifold with the lone pair on nitrogen.

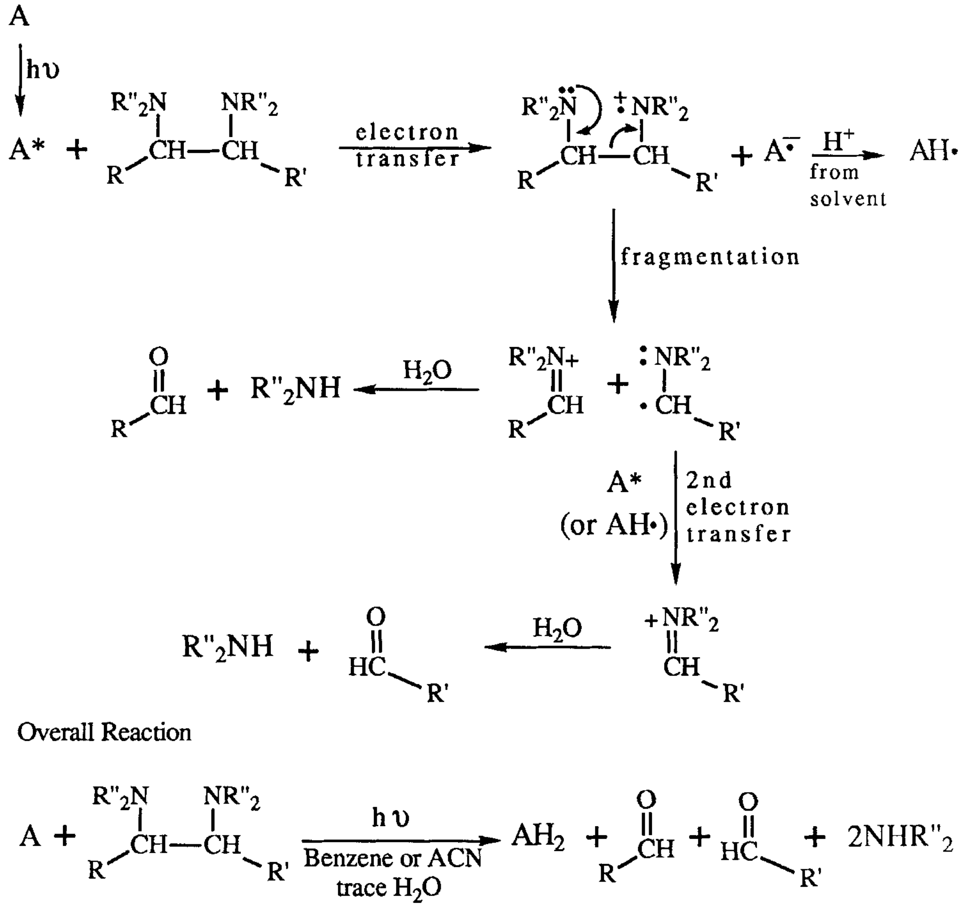
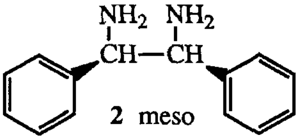


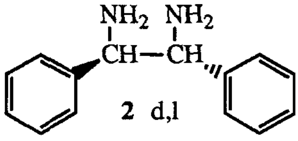
Figure 1 General Mechanism of Diamine Fragmentation

The same trends were observed when the solvent polarity was altered. When a non-polar solvent, such as benzene, was used, the aminoalcohol was more reactive, but in a polar solvent(acetonitrile), the radical ion pair formed by electron transfer is solvent separated rapidly which hinders the deprotonation of the aminoalcohol and thus the diamine was the more reactive by a factor of 3.5:1 for TI in acetonitrile.

The meso and d,l isomers of diamine **2** were independently synthesized[16-20] and taken through similar manipulations as the styrene diamine and aminoalcohol.



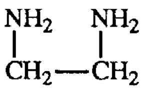
2 meso



2 d,l

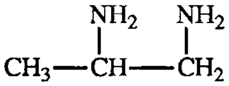
The fragmentation reaction of these compounds was verified by the formation of benzaldehyde in the NMR of irradiated samples of the two isomers with thioindigo as the electron acceptor in benzene-d$_6$. Benzaldehyde production was not visible in the NMR for benzene solutions of DCA and TCA with the isomers of diamine **2**, however, benzaldehyde formation was observed by HPLC with a diode-array UV-vis detector. Direct comparison studies of the reactivity of the two isomers was completed by monitoring the UV-vis bleaching of the different acceptors with extended periods of irradiation. In the case of thioindigo, the two isomers react at essentially the same rate with the only difference being due to the difference in their TI fluorescence quenching constants. The d,l isomer was found to be the better quencher by a factor of 1.6 that of the meso. The relative reactivities were found to be nearly the same regardless of the solvent(either benzene or acetonitrile). With ß-lapachone as the acceptor, the reactivities were again very similar with a slight favoring of the meso isomer by a factor of 1.1 times that of d,l. For the cyanoaromatic cases,(DCA and TCA), the fluorescence quenching studies followed the same trends as were noted for thioindigo. The d,l isomer was the better quencher in both cases with a 1.2:1 ratio for DCA and a 1.3:1 ratio for TCA. However, photoreactions of these systems with monitoring of the UV-vis bleaching of the acceptor demonstrated results very different from the thioindigo and ß-lapachone cases. With TCA in benzene, the reactivity was found to be analogous to what was seen previously for the styrene adducts and for the diamine **2** isomers with TI and ß-lap. The meso isomer was 3 times more reactive than the d,l. For DCA in benzene, neither isomer was seen to cause bleaching of the DCA absorbance. This lack of bleaching of the DCA chromophore, however, does not correspond to a lack of reactivity since when the reaction was monitored by HPLC, benzaldehyde production was found to correspond to the disappearance of the diamine. The lack of change of the DCA acceptor spectroscopically or chromatographically is attributed to trace oxygen regeneration of the original acceptor. Integration of the chromatograms for the DCA cases demonstrated again that there is very little difference in the reactivity of the two isomers. The most pronounced differences in this series of studies were found in the case of the diamine **2** isomers with TCA in acetonitrile. In the cases of TI, ß-lap, and TCA in benzene solution, the bleaching of the acceptor was seen to coincide with the growing in of the dihydroacceptor which absorbs at higher energy shorter wavelengths. Irradiation of a degassed yellow solution of TCA in acetonitrile caused a dramatic color change to occur with a resulting deep blue solution, the decrease of the TCA absorbance was concurrent with the appearance of a large amount of structured absorbance throughout the long wavelength visible spectra. The intensity of the blue color increased with continued irradiation until all of the original TCA absorbance was bleached out. When the sealed tube was exposed to oxygen the blue color disappeared rapidly with the reappearance of the original yellow color which corresponded to a complete regeneration of the initial TCA absorbance. This blue color was later found to correspond to the formation of the anion radical of tetracyanoanthracene stabilized in degassed acetonitrile solution. The EPR spectra of the anion radical was obtained and was found to consist of 55 lines whose hyperfine splitting constants are yet to be determined. The formation of the anion radical was verified by a bulk electrolysis of a degassed TCA solution in an electrochemical cell with a transparent platinum mesh electrode. The solution was allowed to draw current only from the potential corresponding to the first reduction wave of TCA. The UV-vis absorption spectra obtained by this electrochemical method was identical to that observed for the photochemical process and both of these spectra were in agreement with one obtained by an independent laser flash photolysis study of TCA with a toluene donor.[21] Although the TCA is completely recovered, the desired reactivity is still witnessed by the appearance of the benzaldehyde product in the HPLC analysis.

Concurrent with the studies of the stereoisomers of diamine **2**, some aliphatic di-primary amines were examined for their reactivity with the different electron acceptors. The diamines **3** and **4** were subjected to the same types of manipulations as for the aminoalcohols and diamines previously mentioned.



$\overset{\mathrm{NH_2}}{\mathrm{CH_2}}{-}\overset{\mathrm{NH_2}}{\mathrm{CH_2}}$

3



$\mathrm{CH_3}{-}\overset{\mathrm{NH_2}}{\mathrm{CH}}{-}\overset{\mathrm{NH_2}}{\mathrm{CH_2}}$

4

The quenching of thioindigo fluorescence was determined and **4** was found to be the better quencher by a factor of 1.1 times. However, both **3** and **4** were found to be 3 times better quenchers than the diamine **2** isomers. In a comparison photolysis study, the diamine **4** was found to bleach the thioindigo absorbance at a rate two times greater than diamine **3**, but both were 15 times less reactive than either of the isomers of **2**. When the triplet acceptor ß-lap was used, **4** was still favored but the reactivities were 10 times greater than with TI. Product analysis of these systems has yet to be undertaken and thus it would be fortuitous to claim that the bleaching of the acceptors is concurrent with a fragmentation of these diamines, **3** and **4**.

As was previously reported the acceptor is the most important factor influencing the reactivity of aminoalcohols, due to the deprotonation assisted fragmentation. Whereas for the ditertiary amine previously studied, its reactivity was relatively unchanged for changes in acceptor or solvent polarity. The present studies demonstrate further the generality of 1,2-diamines' ability to undergo electron transfer photofragmentation, with little influence from the acceptor used. The most dramatic evidence being shown by the formation of the stable TCA anion radical in acetonitrile solution. This demonstrates that the photoexcited TCA electron acceptor acts as a non-sacrificial reagent or perhaps catalyst for the cleavage of the carbon-carbon bond of 1,2 diamines. This shows that even though a deprotonation assisted pathway is available to the 1,2-diprimary amine **2**, it is not the manifold in which the fragmentation occurs, rather the unassisted pathway involving the lone pair on nitrogen is more likely to be the working mechanism of diamine electron transfer photofragmentation.

In summary, these studies further demonstrate that chemically clean oxidative photofragmentation of 1,2-diamines can occur by a mechanism analogous to that elucidated for aminoalcohols. However, it is evident that the versatility of this reaction is much greater for diamine substrates. Additional studies of other diamine substrates, such as heterocyclic ring compounds and more complete studies of aliphatic diamines should provide more evidence for the understanding of the scope and the utility of this type of reaction.

ACKNOWLEDGEMENTS

We thank the Department of Energy (Grant No. DE-FG02-86ER13504) for support of this research. M. A. Kellett is also grateful for an Arnold Weissberger Fellowship.

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