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TECHNICAL REPORT  
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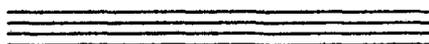
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# SYNTHETIC AND MECHANISTIC STUDIES ON ZINC TETRABENZPORPHYRINS

John W. Cullen  
David E. Remy

August 1992

Final Report  
May 1991 - August 1991



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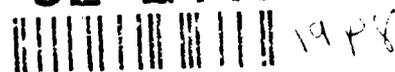
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# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE August 1992	3. REPORT TYPE AND DATES COVERED Final Report - May 91 to August 91	
4. TITLE AND SUBTITLE Synthetic and Mechanistic Studies on Zinc Tetrabenzoporphyrins			5. FUNDING NUMBERS PE: 1L161102 PR: AH5201 WU: AOO AGG CODE: T/B1384	
6. AUTHOR(S) John W. Cullen and David E. Remy			8. PERFORMING ORGANIZATION REPORT NUMBER NATICK/TR-92/021	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Natick Research, Development and Engineering Center Kansas Street, ATIN: SIRNC-YSM Natick, Massachusetts 01760-5020			10. SPONSORING MONITORING AGENCY REPORT NUMBER	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES John Cullen's professional affiliation is Monroe Community College, Rochester, New York 14623.				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release, distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Tetrabenzoporphyrins have been reported to possess very high values for third-order nonlinear optical susceptibility ( $\chi^3$ ). The preparation of meso substituted zinc tetrabenzoporphyrins (TBP's) from isoindole, zinc acetate and aldehydes is described. The scope of the reaction is discussed with regard to several aromatic aldehydes used for the synthesis. Benzaldehydes with electron - withdrawing groups gave little or no product, and sterically hindered aldehydes gave low yields of TBP's that were only partially substituted in the meso positions. Poor yields in these cases are discussed in terms of charge transfer interactions or steric factors in the reactions. A mechanism for the formation of TBP's under these conditions is presented and discussed. The mechanism involved initial condensation of isoindole and the aldehyde to form an isoindolidene which then oligimerizes and cyclizes. Then oxidation occurs to form the fully conjugated TBP. In the oxidation, the aldehyde is proposed to function as a hydride acceptor. Plans for future research in this area are discussed.				
14. SUBJECT TERMS Tetrabenzoporphyrins, Porphyrins, Metalloporphyrins, Nonlinear Optical Materials, Oxidation, Eye Protection			15. NUMBER OF PAGES 18	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED			16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UNLIMITED

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## PREFACE

The work described in this report was authorized under work unit 1L161102AH5202050A00 entitled **Advanced materials** and covers the period from May 1991 to August 1991. The report discusses the synthesis and mechanism of formation of zinc tetrabenzporphyrins.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge the contribution of Drs. R. Willingham, J. Cornell, and D. Alabran. They also want to thank Mr. J. Carlson for key mass spectral data.

SYNTHETIC AND MECHANISTIC STUDIES OF  
ZINC TETRABENZPORPHYRINS

INTRODUCTION

There has long been an interest in these laboratories in developing materials for eye protection to defend the soldier against threats from radiation damage. The development of tunable laser weapons systems increases the possibility of severe damage to the retina of the eye on the modern battlefield. One defense against such systems is the development of nonlinear optical (NLO) materials that can be incorporated into eye protection media. These materials will allow transmission of visible light at ordinary intensities, but will reversibly block transmission at high intensities damaging to the eye.

Nonlinear optics involves the interaction of electromagnetic radiation with materials that can change the frequency, phase, amplitude and other properties of the incident radiation. This interaction causes changes in the physical properties (such as refractive index) of the material. In order to obtain the desired eye protection, materials are needed that produce NLO effects with sufficient magnitude and velocity to block an incoming laser pulse.

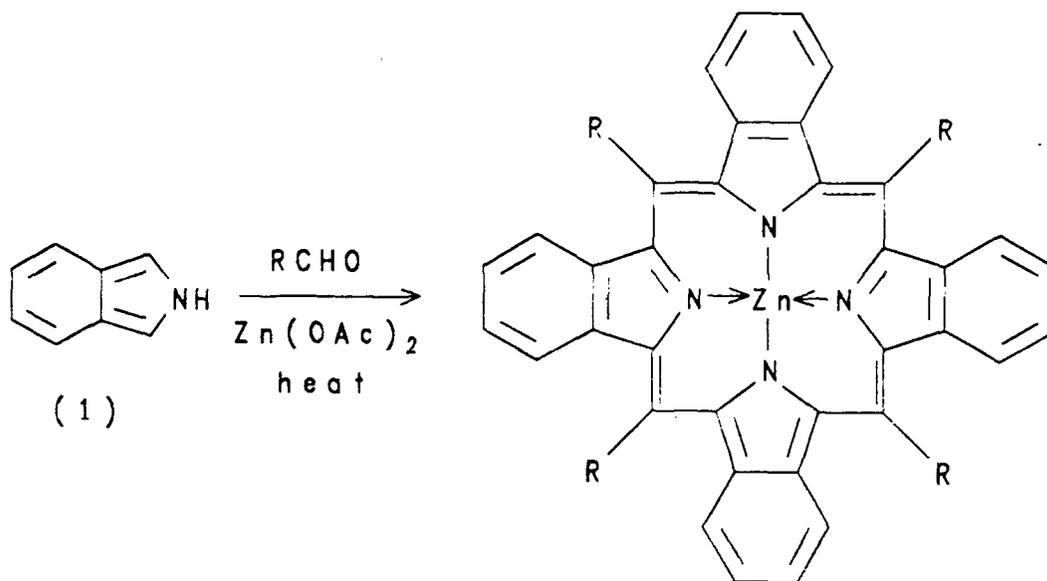
For eye protection, ultrafast (i.e., subpicosecond) response times are required. Ordinary chemical reactions involving rearrangements of atoms or groups of atoms cannot be expected to give a

sufficiently rapid response. However, ultrafast responses should be possible when only the movement of electrons is involved.

In order to give sufficiently large magnitudes of NLO effects, materials should have a large number of very polarizable electrons. This study focuses on the synthesis of substances that have the potential for high third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) values. Third-order nonlinearity results in frequency tripling of the incident radiation and changes in the refractive index of the material. This last property is considered to be the most important for laser eye protection. Current theory suggests that for molecules to exhibit high  $\chi^{(3)}$  values, they should possess centrosymmetry and extensive delocalization of electrons. One class of compounds that meet these criteria and which have recently been shown to exhibit high  $\chi^{(3)}$  values<sup>1</sup> are the metallotetrabenzoporphyrins.

TECHNICAL DISCUSSION

In 1983 D. Remy reported that reaction of isoindole 1 and formaldehyde or benzaldehyde at high temperature under a nitrogen atmosphere in the presence of zinc acetate produces zinc tetrabenzporphyrin (TBP) 2a or zinc 5,10,15,20-tetraphenyltetrabenzporphyrin 2b in moderate yield.<sup>2</sup>

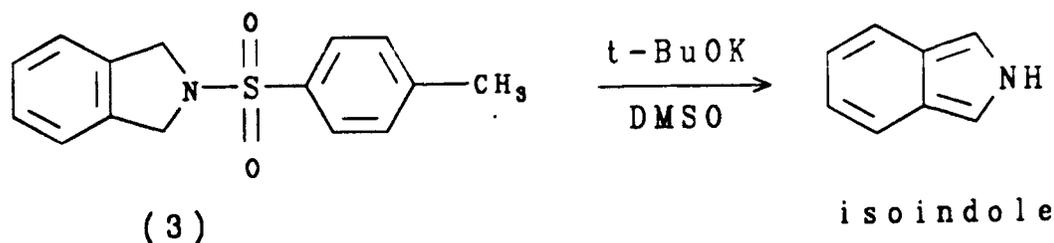


(2a) R = H

(2b) R = Phenyl

This synthesis of tetrabenzporphyrins is analogous to the Rothmund synthesis<sup>3,4</sup> of porphyrins from pyrrole and aldehydes. We wish to report on our efforts to extend the scope of this reaction and to use these observations to comment on a possible mechanism for this reaction.

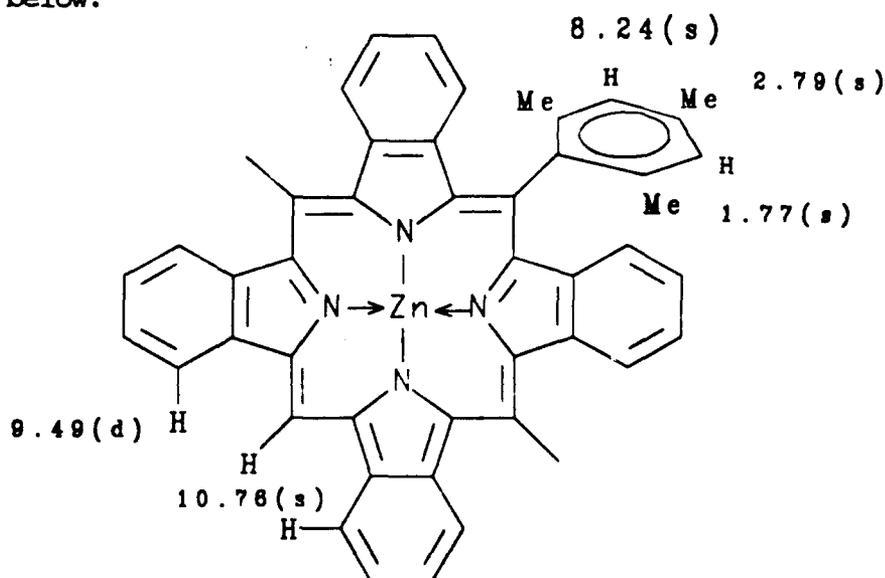
Isoindole (unlike pyrrole) is very labile and rapidly decomposes by polymerization at room temperature. In solution it is sufficiently stable that it can be used immediately after generation to prepare TBP's. Initially isoindole was prepared by retro-Diels-Alder reaction of 1,2,3,4-tetrahydronaphthalen-1,4-imine.<sup>5</sup> Now we are using a more convenient synthesis in which isoindole is prepared from 2-(p-toluenesulfonyl)dihydroisoindole **3** by reaction with potassium tert-butoxide in dimethylsulfoxide.<sup>6</sup>



We have extended the scope of the reaction to prepare a variety of substituted zinc TBP's **2** including those where R is methyl, 4-methylphenyl, 4-methoxyphenyl, 4-dimethylaminophenyl, 3-fluorophenyl and 4-chlorophenyl in moderate yields from the corresponding aldehydes. The structure of the products was confirmed by their mass spectra, UV/visible spectra and, in some cases, by their <sup>1</sup>H and <sup>13</sup>C NMR spectra. Reaction with 4-cyanobenzaldehyde or 4-nitrobenzaldehyde gave only traces of TBP product. With 4-cyanobenzaldehyde the major product was a dark purple solid which was insoluble in all solvents and appears to be polymeric in nature.

Aldehydes with large, bulky aryl groups (1-naphthaldehyde and 9-phenanthraldehyde) gave poor results. Yields were low and several

green bands were observed when the crude products were subjected to thin-layer chromatography. These materials also degraded relatively rapidly, becoming brown on exposure to air after several days. A tetrabenzporphyrin was isolated in 2% yield from the reaction with 2,4,6-trimethylbenzaldehyde (mesitaldehyde). The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of the material showed that it was only partially substituted with mesityl groups in the meso positions. NMR assignments are shown below.



That the product is at least partially mesitylated in the meso positions is seen in the chemical shift of the methyl groups. The ortho methyls absorb at 1.77 ppm (compared with 2.54 ppm in mesitaldehyde), indicating that they lie in the shielding region of the TBP pi-system. That some meso positions remain unsubstituted is shown by the presence of a singlet at 10.76 ppm (the meso protons in 2a absorb at 11.28 ppm in pyridine- $d_5$ ). In addition there is a doublet at 9.49 ppm, which is assigned to the protons on the benzo rings nearest the meso H's. In zinc TBP 2a these protons absorb at 9.80 ppm,

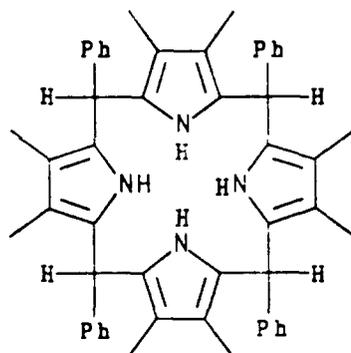
whereas in the meso tetraphenyl derivative 2b they are shifted to 7.22 ppm because they are in the shielding region of the phenyl groups. We attribute the multiplicity of products with other hindered aldehydes to the presence of partially substituted TBP's.

It is well known in the simple porphyrin series that addition of metal salts such as zinc acetate improves the yields of porphyrins considerably.<sup>7</sup> The usual explanation is that linear oligomerization of pyrrole units is competing with cyclization to give porphorinic products and that chelation of the nitrogen atoms to the metal shifts the equilibrium towards cyclization. In our hands the best yields of TBP's are obtained when one mole of zinc acetate is used per mole of isoindole. Lower amounts of zinc acetate give lower yields. Attempts to run the reactions using zinc chloride or zinc oxide gave little or no TBP's. Surprisingly, poor yields were also obtained when nickel (II) or copper (II) acetate were employed.

#### Mechanistic Considerations

In view of the complexity of the reaction and the severity of the conditions used (ca. 400°C), it is difficult to state presently much about the mechanism of zinc TBP formation with any degree of certainty. Nonetheless, a tentative mechanism is presented below, based on the observations noted previously, knowledge of the chemistry of isoindole and mechanistic studies on porphyrin formation.

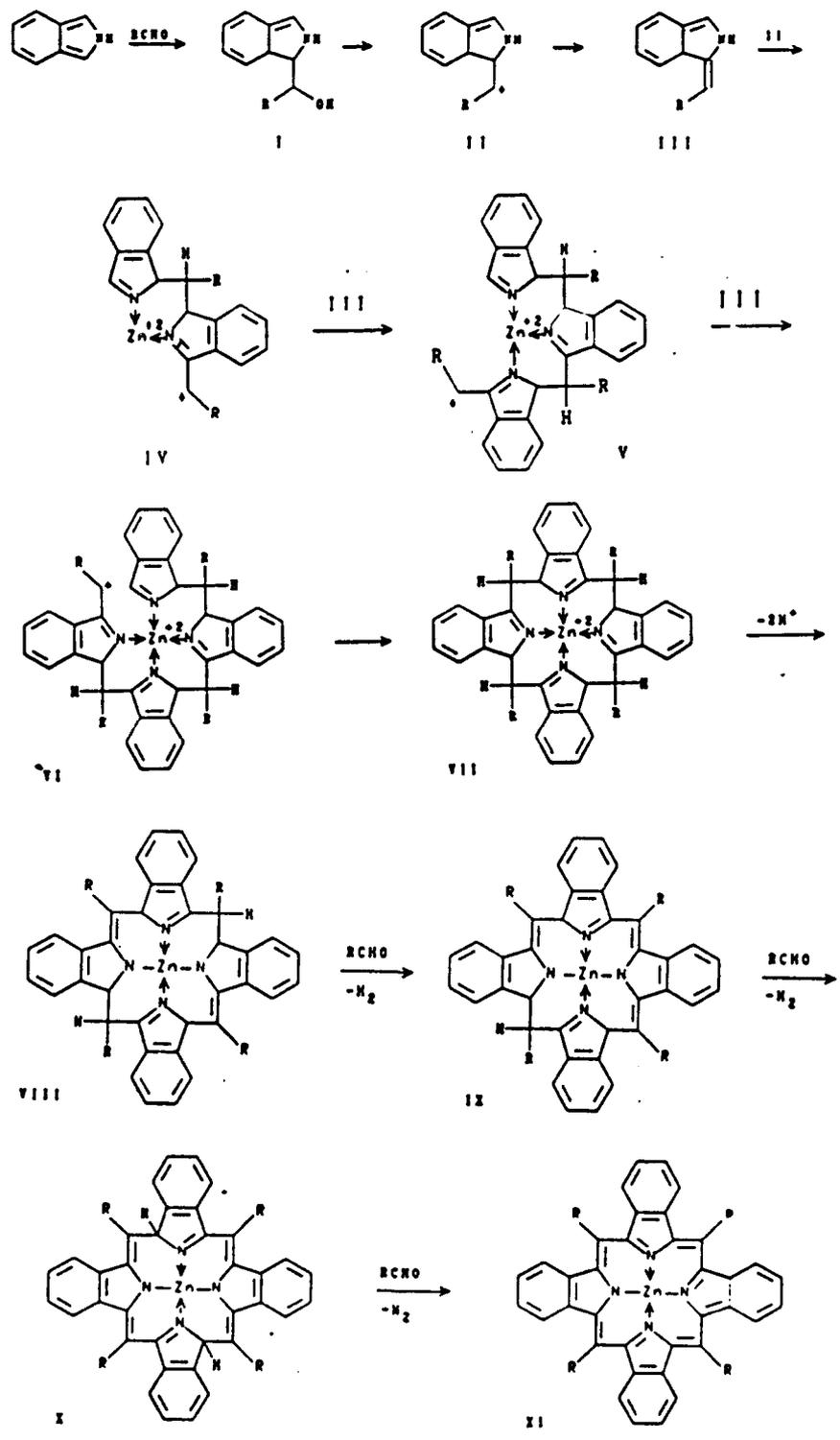
There have been a number of attempts to elucidate the mechanism of porphyrin formation in the Rothemund synthesis. It is clear that both condensation and oxidation steps are involved in the conversion of pyrroles to porphyrins. There are several lines of evidence that indicate that condensation occurs prior to oxidation. Adler, Longo and Shergalis<sup>8</sup> showed that in pyrrole-benzaldehyde reactions carried out in air which require 6-8 h to go to completion that 80% of the water formed can be detected in the first 20 min of the reaction. Dolphin<sup>9</sup> has isolated the porphyrinogen below from the reaction of 3,4-dimethylpyrrole and benzaldehyde.



On the following page, a possible mechanism for the formation of zinc TBP's from isoindole, aldehydes and zinc acetate is presented. The reaction is visualized as progressing through three stages:

1. Initial nucleophilic attack by the electron-rich isoindole on the aldehyde (which may be activated by prior coordination of carbonyl oxygen to zinc) to give the alcohol I after proton transfer. The alcohol can then dehydrate to form the isoindolidene III via carbocation II.

Possible Mechanism of Zinc Tetrabenzporphyrin Formation



2. The oligomerization process is believed to proceed by reaction of intermediates II and III to form the diisoiindolymethane carbocation IV (almost certainly coordinated to zinc). Two consecutive attacks by the isoindolidene III on the corresponding cations generates the tetramer VI, which then cyclizes in the manner shown. Loss of two protons gives the tetrabenzporphrinogen VIII. It is possible that one or both deprotonations occurs before the cyclization step.

3. The final stage of this mechanism is oxidation of the tetrabenzporphrinogen to the tetrabenzporphyrin. This involves loss of six hydrogen atoms. An ionic mechanism involves the aldehyde acting as a hydride acceptor with loss of a proton. Repetition of this step through intermediates such as IX and X yields the completely conjugated tetrabenzporphyrin XI. The driving force for these oxidation steps is the aromatization of the system.

Undoubtedly, this mechanism is not correct in all its details, but it does provide a rational explanation for the synthesis of TBP's from isoindole under the given reaction conditions. At present we have no evidence for the presence of any of these reaction intermediates.

There are several points which need to be examined in order to work out the details of the mechanism. One is the identity of the uncyclized oligomers. The mechanism presented shows a stepwise addition of isoindole units. Another possibility is the coordination of two bisisoiindoyl units to zinc followed by cyclization. Such mechanisms have been postulated in the simple porphyrin systems.

An important issue is the nature of the oxidizing agent. Our mechanism involves the aldehyde acting as a hydride acceptor. The well-known Cannizzaro reaction provides precedent that aldehydes can in fact function in this manner. Other possible oxidizing agents are atmospheric oxygen or zinc acetate. Adler et al.<sup>10</sup> showed that in the formation of meso-tetraphenylporphyrin from benzaldehyde and pyrrole under aerobic conditions, the oxidizing equivalents for the reaction were supplied entirely by atmospheric oxygen. Our reactions are usually carried out under a sweep of dry nitrogen. In the reaction with 4-methoxybenzaldehyde, recent experiments have shown that the isolated yield of the TBP product increases from 10% to 17% if the reaction is done using excess aldehyde (2.5 moles per mole of isoindole rather than 1.0) or if the reaction is done under a sweep of air rather than nitrogen.

The lack of complete meso substitution observed with mesitaldehyde and other aldehydes can be explained by postulating an alternative reaction pathway for intermediates such as VII, VIII or IX. Loss of the aryl group (perhaps as a free radical) under these conditions may compete with loss of hydrogen and lead to partially substituted products. Indeed we have observed that heating meso-tetraphenyl TBP at 400°C for 24 h under nitrogen results in loss of phenyl groups and the appearance of meso hydrogens in the <sup>1</sup>H NMR spectrum.

As indicated earlier, 4-cyano and 4-nitrobenzaldehyde give little or no TBP product when reacted under the usual conditions. Both of these aldehydes are rather good pi-acceptors. With these aldehydes, formation of a charge-transfer complex between isoindole and the electron-deficient aldehyde may compete with or inhibit the condensation reactions leading to TBP's. Isoindole has been reported to react with 1,3,5-trinitrobenzene to give a deep red color that has been attributed to pi-complexation.<sup>11</sup>

## SUMMARY, RECOMMENDATIONS AND CONCLUSIONS

Reaction of isoindole with aldehydes in the presence of zinc acetate at high temperatures gives zinc TBP's in moderate yields. Initially the parent 2a and meso-tetraphenyl derivative 2b were prepared. The reaction has been extended to other aromatic aldehydes, and it is possible to define the scope of this reaction with regard to the structure of the aldehyde. Benzaldehyde and most monosubstituted benzaldehydes give acceptable yields. The two types of aldehydes that gave very poor results were relatively bulky ones (presumably due to steric hindrance in the meso positions of the TBP products) and those with a powerful electron-withdrawing group which may be forming charge-transfer complexes with isoindole.

A mechanism has been proposed which accounts for the formation of zinc TBP's under the reaction conditions. Additional effort will be required to elucidate the details of the mechanism. Identification of the intermediates and by-products of the reaction would be useful in this regard. These studies should help to optimize yields.

Additional porphyrin derivatives should be prepared in order to determine how structural modification will affect the Chi-3 values. Efforts are currently underway to prepare and test porphyrins with even more extended pi-systems: tetranaphthoporphyrins and tetraphenanthroporphyrins. It is hoped that the increased electron delocalization will boost the Chi-3 value significantly.

Another modification that should be examined is to prepare and test TBP's that are complexed to metals other than zinc. Zinc can be removed easily by treatment with trifluoroacetic acid and other metals inserted by treatment with the metal acetate in methanol. It would be informative to study the variation of Chi-3 values with the size, oxidation state, electron configuration and other properties of the metal.

Efforts are in progress to prepare functionalized TBP's with the goal of incorporating them into polymer structures. Current efforts are focused on the synthesis of zinc tetra(4-hydroxyphenyl) or (4-aminophenyl)TBP and subsequent functionalization of the hydroxyl or amino groups by alkylation or acylation reactions. At this time we have evidence for the formation of zinc tetra(4-hydroxyphenyl) TBP and are attempting to confirm its structure.

This document reports research undertaken at the US Army Natick Research, Development and Engineering Center and has been assigned No. NATICK/TR-~~9~~1011 in the series of reports approved for publication.

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