

thalide to polymer-bound titanocene dichloride resulted in the formation of species with two distinctly different esr signals of comparable intensity near $g = 2$.¹⁰ These data suggest that both stages of reduction yield paramagnetic species. Treatment of monomeric benzyltitanocene with sodium naphthalide under identical conditions yields solutions containing a rapidly disappearing paramagnetic species and mediocre catalytic ability. These observations support the suggestion that dimerization of the reduced titanocene complexes has been avoided by polymer attachment.

Acknowledgments. The authors wish to thank the Dow Chemical Co. for the gift of the polystyrene beads used in this work. Carl Gibbons thanks Dow Chemical Co. for support while completing this research. This work was also supported in part under NSF Grant GP 17422X.

(10) H. H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

(11) On leave from The Dow Chemical Co., Midland, Mich.

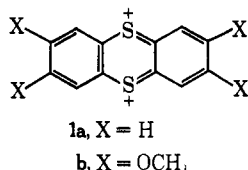
Robert H. Grubbs,* Carl Gibbons,¹¹ LeRoy C. Kroll
Wesley D. Bonds, Jr., C. H. Brubaker, Jr.
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Received November 29, 1972

2,3,7,8-Tetramethoxythianthrene Dication. An Isolable Thianthrene Dication

Sir:

There is considerable theoretical interest in potentially aromatic compounds formally derived from aromatic hydrocarbons or ions (or perhaps better said Hückel systems)¹ in which one or more carbon atom is replaced by one or more heteroatom. Thianthrene dication **1a** is one such system. If d orbitals are neglected then



thianthrene dication is derived from anthracene because the number of atomic orbitals capable of forming π molecular orbitals and the number of electrons to be accommodated in these orbitals are the same in both systems.² However, if sulfur uses pd^2 hybrid atomic orbitals^{2,3} then thianthrene dication is derived from dibenzo[*a,e*] cyclooctatetraene dication.

Thianthrene dication is of interest not only for theoretical reasons but also because it has been suggested as an intermediate in the reactions of thianthrene cation radical with nucleophiles.⁴ This suggestion, however, has been challenged recently.⁵

(1) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972).

(2) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966.

(3) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

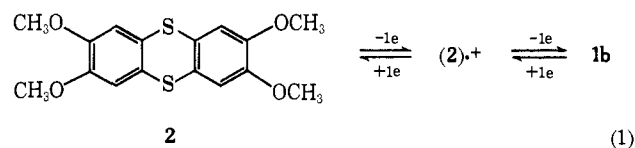
(4) (a) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 1872 (1969); (b) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969); (c) J. J. Silber and H. J. Shine, *ibid.*, **36**, 2923 (1971); (d) H. J. Shine and J. J. Silber, *J. Amer. Chem. Soc.*, **94**, 1026 (1972).

(5) V. D. Parker and L. Ebersson, *ibid.*, **92**, 7488 (1970), but see also L. Marcoux, *ibid.*, **93**, 537 (1971) for limitations of the rotating disk electrode technique.

Dissolution of thianthrene sulfoxide in concentrated sulfuric acid gives rise reportedly⁶ to the dication **1a**. The evidence for this contention is the observed i factor of 5 and the isolation of ¹⁸O-labeled thianthrene sulfoxide after pouring a solution of the dication onto ice prepared from ¹⁸O-labeled water. No direct evidence for dication **1a** has been presented nor has dication **1a** been isolated.

This communication reports the isolation of a substituted thianthrene dication and the evidence for the assigned structure. The dication of 2,3,7,8-tetramethoxythianthrene (**1b**) could be prepared from 2,3,7,8-tetramethoxythianthrene⁷ in any of three ways: (1) anodic oxidation, (2) oxidation by perchloric acid, and (3) oxidation by oxygen in the presence of aluminum chloride.

Cyclic voltammetric studies on 2,3,7,8-tetramethoxythianthrene in purified acetonitrile⁸ 0.1 *M* in tetra-*n*-butylammonium perchlorate show three oxidation waves with half-wave potentials at +0.54, +0.79, and +1.20 V *vs.* silver|saturated silver nitrate (acetonitrile). The first oxidation is reversible at moderate scan rates (0.435 V/sec) but, unlike the case of thianthrene,⁹ the second oxidation process is also reversible at the moderate scan rate. The scan rate independent separations of the anodic and cathodic waves for both processes (both 60 mV) suggest¹⁰ that each step involves the transfer of one electron. These reversible oxidation processes may be accounted for by the reaction shown in eq 1.



Controlled potential electrolysis of 2,3,7,8-tetramethoxythianthrene in acetonitrile 0.1 *M* in tetra-*n*-butylammonium perchlorate was complicated by the limited solubility of the products. However, this problem was eliminated by use of nitromethane¹¹ as solvent and anhydrous magnesium perchlorate (at saturation) as supporting electrolyte. With these conditions, the waves due to the two reversible oxidation processes observed in acetonitrile overlapped. Nevertheless, sufficient separation was obtained in an epr cavity cell equipped with a platinum gauze electrode so that two waves were observed at half-wave potentials of +0.6 and +0.8 V *vs.* silver|saturated silver nitrate (nitromethane). Electrolysis at the potential of the first wave produced a green solution which gave an epr signal. At high resolution a complex spectrum whose g value and hyperfine splitting were consistent with that expected for the resonance of the cation radical of

(6) (a) H. J. Shine and D. R. Thompson, *Tetrahedron Lett.*, 1591 (1966); (b) H. J. Shine in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, Chapter 6.

(7) K. Fries, H. Koch, and H. Stukenbrock, *Justus Liebigs Ann. Chem.*, **478**, 162 (1929).

(8) C. K. Mann in "Electroanalytical Chemistry," A. J. Bard, Ed., Vol. 3, Marcel Dekker, New York, N. Y. 1969.

(9) (a) C. Barry, G. Cauquis, and M. Maurey, *Bull. Soc. Chim. Fr.*, 2510 (1966); (b) W. Schroth, R. Borsdorf, R. Herzsuh, and J. Seidler, *Z. Chem.*, **10**, 147 (1970).

(10) (a) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964);

(b) R. S. Nicholson and I. Shain, *ibid.*, **37**, 178 (1965).

(11) J. D. Voorhies and E. J. Schurdak, *ibid.*, **34**, 939 (1962).

2,3,7,8-tetramethoxythianthrene was observed.^{6b,12,13} Electrolysis of a nitromethane solution containing 2,3,7,8-tetramethoxythianthrene and saturated with anhydrous magnesium perchlorate at a constant potential of +1.00 V vs. silver|saturated silver nitrate (nitromethane) gave an apparent "n" value of 2.06. Thus, two electrons were removed from each molecule of 2,3,7,8-tetramethoxythianthrene to give a sapphire blue solution ($\lambda_{\max} = 710 \text{ nm}$)¹⁴ of dication **1b**.

Oxidation of 2,3,7,8-tetramethoxythianthrene by perchloric acid gave the corresponding dication diperchlorate as a dark blue solid. This material dissolved in nitromethane saturated with aluminum chloride was devoid of an epr signal and its absorption in the visible was very similar to the dication solution prepared by controlled potential electrolysis. A weighed amount of the solid dication diperchlorate was added to a mixture of nitromethane and water. The aqueous phase after separation was neutralized and analyzed for perchlorate ion by use of a perchlorate ion specific electrode.¹⁵ The amount of perchlorate ion found by this analysis was consistent with a formula of $\text{C}_{16}\text{H}_{16}\text{O}_4\text{S}_2 \cdot 2\text{ClO}_4$ for the solid. Another sample of the solid dication diperchlorate dissolved in nitromethane containing anhydrous magnesium perchlorate was titrated with a solution of 2,3,7,8-tetramethoxythianthrene (**2**) and anhydrous magnesium perchlorate in nitromethane. The amount of 2,3,7,8-tetramethoxythianthrene required to reach the endpoint determined visually by the color change was consistent with the reaction shown in eq 2. The green solution resulting



from this titration ($\lambda_{\max} = 765 \text{ nm}$) unlike its precursors gave an epr signal. The epr spectrum was the same as that obtained from the 2,3,7,8-tetramethoxythianthrene cation radical formed by controlled potential electrolysis of 2,3,7,8-tetramethoxythianthrene.

Oxygen bubbled into a solution of 2,3,7,8-tetramethoxythianthrene in nitromethane saturated with aluminum chloride gave a sapphire blue solution of dication **1b**. The blue solution was not obtained in the absence of oxygen. The visible absorption spectrum of this solution was virtually the same as the blue solutions obtained by anodic or perchloric acid oxidation of 2,3,7,8-tetramethoxythianthrene. The nmr spectrum of this blue solution showed two broad singlets at δ 6.6 (12 H) and 8.4 (4 H) ppm downfield from external tetra-

(12) (a) J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **75**, 4115 (1953); (b) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955); (c) C. MacLean and J. H. van der Waals, *ibid.*, **27**, 827 (1957); (d) A. Fava, P. B. Sogo, and M. Calvin, *J. Amer. Chem. Soc.*, **79**, 1078 (1957); (e) W. C. Needler, *Diss. Abstr.*, **22**, 3873 (1962); (f) H. J. Shine and L. Piette, *J. Amer. Chem. Soc.*, **84**, 4798 (1962); (g) M. Kinoshita and H. Akamatu, *Bull. Chem. Soc. Jap.*, **35**, 1040 (1962); (h) M. Kinoshita, *ibid.*, **35**, 1137 (1962); (i) E. A. C. Lucken, *J. Chem. Soc.*, 4963 (1962); (j) H. J. Shine, C. F. Dais, and R. J. Small, *J. Chem. Phys.*, **38**, 569 (1963); (k) W. Rundel and K. Scheffler, *Tetrahedron Lett.*, 993 (1963); (l) E. A. C. Lucken, *Theor. Chim. Acta*, **1**, 397 (1963); (m) H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, **29**, 21 (1964); (n) Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **40**, 2539 (1967); (o) G. Vincow in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, pp 190-193; (p) H. J. Shine and P. D. Sullivan, *J. Phys. Chem.*, **72**, 1390 (1968); (q) P. D. Sullivan, *J. Amer. Chem. Soc.*, **90**, 3618 (1968).

(13) Apparently, Fries and coworkers⁷ prepared crystalline salts of the 2,3,7,8-tetramethoxythianthrene cation radical.

(14) Thianthrene dication in 100% sulfuric acid is reported to have absorption maxima at 311 and 502 nm.

(15) H. James, G. Carmack, and H. Freiser, *Anal. Chem.*, **44**, 856 (1972).

methylsilane.¹⁶ The nmr spectrum is easily reconciled with structure **1b**.^{16,17} The very markedly deshielded methyl groups indicate considerable delocalization of the positive charges from the rings to the oxygen atoms.

The data strongly support the thesis that oxidation of 2,3,7,8-tetramethoxythianthrene in each of the three ways studied gives the corresponding dication **1b**.

Acknowledgment. Support of this research by the National Institutes of Health, the National Science Foundation, and the Mobil Foundation is gratefully acknowledged.

(16) The chemical shifts depended on the concentration of the dication. Concentration dependent chemical shifts have been reported for the closely related thioxanthylum perchlorate: H. J. Shine and L. Hughes, *J. Org. Chem.*, **31**, 3142 (1966).

(17) (a) T. E. Young and P. H. Scott, *ibid.*, **30**, 3613 (1965); (b) H. J. Shine, L. Hughes, and D. R. Thompson, *Tetrahedron Lett.*, 2301 (1966); (c) K. Dimroth, W. Kinzebach, and M. Soyka, *Chem. Ber.*, **99**, 2351 (1966); (d) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 1558 (1967); (e) B. Föhlisch and D. Krockenberger, *Chem. Ber.*, **101**, 3990 (1968); (f) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969); (g) Z. Yoshida, S. Yoneda, T. Sugimoto, and O. Kikukawa, *Tetrahedron Lett.*, 3999 (1971).

Richard S. Glass,* William J. Britt
William N. Miller, George S. Wilson

Department of Chemistry, The University of Arizona
Tucson, Arizona 85721

Received September 16, 1972

A Convenient General Method of Dehydrogenation Using the Alkylolithium- *N,N,N',N'*-Tetramethylethylenediamine Complex¹

Sir:

Dehydrogenation is frequently the final step in the synthesis of polycyclic aromatic molecules. However, the traditional methods are seldom completely satisfactory due to the facility of competing secondary processes. We now report an efficient and convenient general method of aromatization, utilizing the alkylolithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex.² A significant feature of the method is the intermediacy of the dianions of polycyclic hydrocarbons, the first examples of such to be generated *via* double proton abstraction, with the recent exceptions of the acenaphthylene and naphthalene^{3a} dianions.^{3b}

Initial experiments were conducted with *cis*-9-ethyl-10-methyl-9,10-dihydroanthracene (**1b**) selected as a challenge on the basis of its unsatisfactory behavior with other methods.⁴ In a typical experiment, a solution of *n*-butyllithium (20 mmol) in hexane was introduced by syringe into a solution of **1b** (5 mmol) in dry cyclohexane (30 ml) and TMEDA (15 ml) and the resulting deep red solution of the monoanion brought to reflux, whereupon the color changed to the intense purple characteristic of the dianion. After 1 hr at reflux, the mixture was allowed to cool (5 min) and the color discharged by the addition of anhydrous cad-

(1) This work was supported by U. S. Public Health Service Grant CA 11, 968.

(2) C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965).

(3) (a) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7339, 7346 (1972); (b) L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *ibid.*, **94**, 985 (1972).

(4) Numerous attempts with other reagents (*e.g.*, sulfur, palladium on charcoal, AlCl_3 , I_2 , FeCl_3 , SbCl_5 , DDQ, trityl perchlorate, etc.) led to unsatisfactory yields of products difficult to purify.