affords a mixture of the *cis*- and *trans*-methoxymercurials **5** and **6** in a ratio of 19:81. However, when methylene chloride is utilized as the solvent,[8] with 1 equiv of methanol as the attacking nucleophile, the *cis*-methoxymercurial **5** is formed to the exclusion of the trans adduct **6**. By contrast, utilization of dioxane as the solvent and methanol as the nucleophile resulted in a stereospecific synthesis of the *trans*-methoxymercurial **6**. These data strongly suggest that the mercurinium ion intermediate **2** involved in these reactions is solvated by methanol in methylene chloride solvent. Thus, when methanol is present in limiting quantity, collapse of the solvated mercurinium ion from the front side results in exclusive cis addition. However, with the donor solvent dioxane, methanol is displaced from the primary solvent shell surrounding the mercurinium ion and exclusive trans attack by free methanol in solution on **2** prevails.

The concentration of ^{+}HgX, the rate of reaction, and the product composition are also influenced by the polarity of the solvent. Thus, in dioxane solvent, or when 2 equiv of methanol are present in dioxane, the oxymercuration of **1** with mercuric acetate affords the *cis*-2-acetoxymercuri acetate **3** as the major product in marked contrast to the results with mercuric nitrate. Similarly, in methylene chloride the addition of mercuric acetate to **1**, in the absence of methanol, results in essentially a stereospecific (98%) cis addition. Addition of 1 equiv of methanol to the methylene chloride solvent affords only 17% of **5** and **6**. With the more ionic mercuric nitrate as the electrophilic reagent and acetic acid as the added nucleophile, approximately equal amounts of **3** and **4** are produced in both dioxane and methylene chloride solvent.

Mercurinium ions derived from strained olefins should be relatively short lived if relief of strain cannot be attained on forming an olefin π complex.[5c] Therefore, cis oxymercurials may arise by attack of the displaced ligand X^- on **2** before solvent separation of the intimate ion pair can occur. We therefore suggest that in the present study both cis and trans oxymercurials are derived from a common intermediate, the solvated mercurinium ion **2**, and that the product composition is a function of a ligand effect on the mercury.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to Merck and Co. for support of this work.

(8) Dissolution of $Hg(NO_3)_2$ in CH_2Cl_2 is not effected until the olefin is added, suggesting the formation of an olefin-solvated mercuric ion intermediate. An additional ~16 hr was required for complete reaction.

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Mono-, Di-, and Trications of Hexamethoxytriphenylene. A Novel Anodic Trimerization

Sir:

We report a new synthesis of triphenylene cations from the anodic oxidation of ethers of pyrocatechol in media containing trifluoroacetic acid (TFA). The cation radical **1** is remarkably stable in TFA or dichloromethane while dication **2** shows limited stability in TFA or TFA–$HFSO_3$ and the trication **3** is only observable at temperatures lower than about −50° in TFA–$HFSO_3$. The dication is particularly interesting since it is a ground-state triplet as predicted from theoretical considerations.

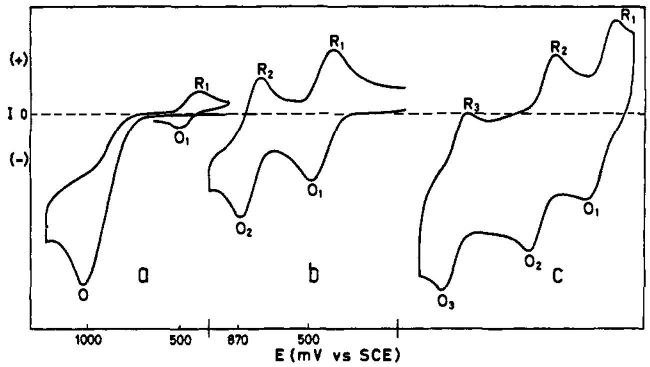
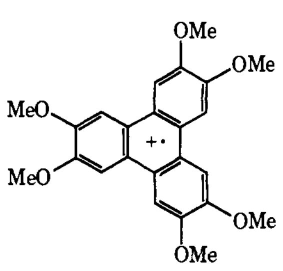


Figure 1. Cyclic voltammograms of (a) veratrole in CH_2Cl_2–TFA (9:1), (b) HMT in TFA, and (c) HMT cation radical in TFA–$HFSO_3$ (1:1). Supporting electrolyte was Bu_4BF_4 and the voltage sweep rate was 150 mV/sec. No reference electrode was used in c.



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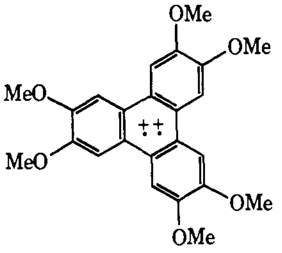

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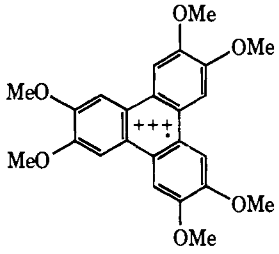

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The reaction resulting in the formation of **1** is illustrated by the cyclic voltammogram of veratrole in dichloromethane–TFA (9:1) containing tetra-*n*-butylammonium fluoroborate (Figure 1a). The initial oxidation peak (O) corresponds to a $^{7}/_{3}$ electron oxidation of veratrole to **1** which is reduced at R_1 to the uncharged hexamethoxytriphenylene (HMT) which is oxidized to **1** at O_1. The use of TFA and dichloromethane–TFA for the anodic generation of cation radicals has recently been described.[1,2]

Figure 1b is the cyclic voltammogram of HMT in TFA. In addition to the R_1–O_1 couple in Figure 1a, the reversible oxidation of **1** to **2** can now be seen by the couple, O_2–R_2. No evidence for a further oxidation of **2** could be obtained in this medium. However, when

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(1) O. Hammerich, N. S. Moe, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 156 (1972).

(2) U. Svanholm and V. D. Parker, *Tetrahedron Lett.*, 471 (1972).

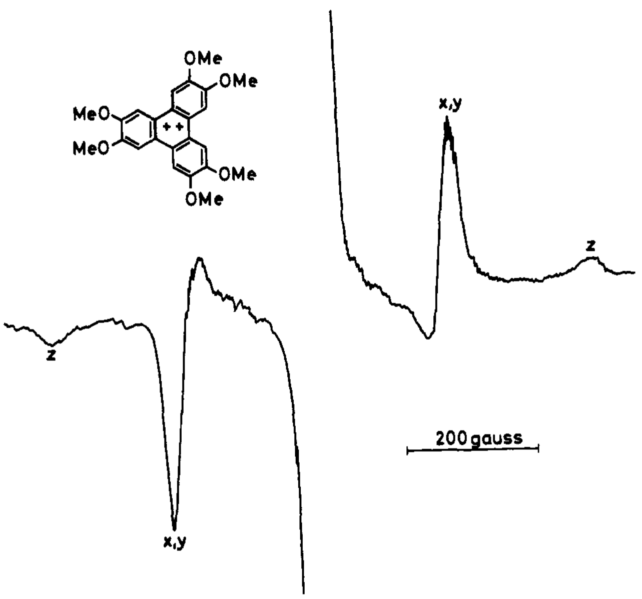


Figure 2. High-field ($\Delta m_s = 1$) esr spectrum of **2**. The central line is due to the monocation.

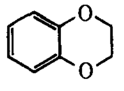
HMT was oxidized to **1** in TFA and the solution then diluted with an equal volume of $HFSO_3$, the room temperature cyclic voltammogram indicated that **2** undergoes further irreversible oxidation. On cooling the solution to −70°, the reversible oxidation of **2** to **3** was observed (Figure 1c). It is interesting to note that the peak separation between oxidation to **1** and **2** is about 300 mV (O_2–O_1) while the peak separation between oxidation to **2** and **3** is 450 mV (O_3–O_2), implying that **3** is considerably more energetic relative to **2** than **2** is to **1**.

In order to observe the esr spectrum of **2**, the best method of generation was found to be low-temperature mixing of a dichloromethane solution of HMT with $SbCl_5$. The esr spectrum of **2** in a frozen dichloromethane–$SbCl_5$ matrix at −196° is shown in Figure 2. Detailed analyses of the line shape of triplet species in rigid media have been reported.[3] The esr spectra of triplet states are usually analyzed in terms of zero-field splitting parameters D and E from the spin Hamiltonian

$$\mathcal{H} = \beta g\bar{H}\bar{S} + DS_z^2 + E(S_x^2 - S_y^2)$$

From our spectrum (Figure 2) we conclude that $D = 0.038\ \text{cm}^{-1}$ and $E \simeq 0$, thus reflecting the trigonal symmetry of the parent molecule. In line with this analysis, zero-field splitting parameters of the same order of magnitude have been reported for the triplet state of triphenylene dianion.[4]

With regard to the preparative aspects of the anodic trimerization, we have observed quantitative 2.3-e coulometry for the anodic oxidation of veratrole in TFA. The peak current for the reduction of cation radical **1** corresponds to that observed from oxidation of the calculated concentration of HMT in the same medium. Thus, the reaction appears to be quantitative on the voltammetric concentration scale (1 m*M*). On a larger scale we have succeeded in the isolation of HMT in about 50% yield. The structure of HMT was definitely established by nmr and ir analysis as well as the melting point as compared to that of the known compound.[5] In addition to veratrole, we have observed the formation of the cation radical of the corresponding triphenylene during oxidation of the cyclic ether **4**. Anodic trimerizations are very rare; two other examples recently reported are the trimerization of anthracene[6] and mesitylene.[7]



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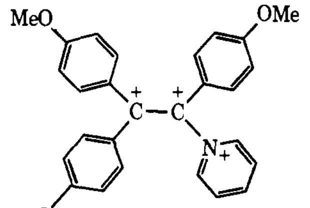
To our knowledge, our observation of the esr spectrum of the dication **2** is the first evidence for an aromatic triplet dication. The trication **3** is also to our knowledge the first conjugated aromatic trication. The trication **5**[8] as well as several in which the charges are isolated by saturated carbon[9] such as **6** have been reported. Our application of low-temperature voltammetry to observe **3** illustrates the usefulness of this technique in the observation of unstable intermediates and it is indeed surprising that this technique has so seldomly been used. We are continuing our studies in related systems in an attempt to observe other triplet dications.



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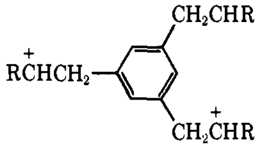

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[3] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[4] J. L. Sommerdijk and E. de Boer, *ibid.*, **50**, 4771 (1969).

[5] M. Piattelli, E. Fattorusso, R. A. Nicolaus, and S. Magno, *Tetrahedron*, **21**, 3229 (1965).

[6] V. D. Parker, *Acta Chem. Scand.*, **24**, 2757 (1970).

[7] K. Nyberg, *ibid.*, **25**, 2499 (1971).

[8] V. D. Parker and L. Eberson, *Chem. Commun.*, 451 (1969).

[9] H. Baumgartel, EUCHEM Conference, Ronneby, Sweden, June 1971.

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Raman Circular Dichroism. Its Observation in α-Phenylethylamine

Sir:

It has occurred to us and others[1-3] that the observation of circular dichroism in the vibrational spectra of chiral molecules could provide a new and powerful probe into their electronic and stereochemical structures. This note describes what we believe is the first successful attempt to measure circular dichroism in the Raman effect. We measured the effect as follows.

The basic equipment consisted of a Beckman Model 700 Raman spectrophotometer and a Carson Model 200 argon laser. The Raman spectra were recorded

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[1] C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968).

[2] L. D. Barron and A. D. Buckingham, *Mol. Phys.*, **20**, 1111 (1971).

[3] A. J. McCaffery, private communication.