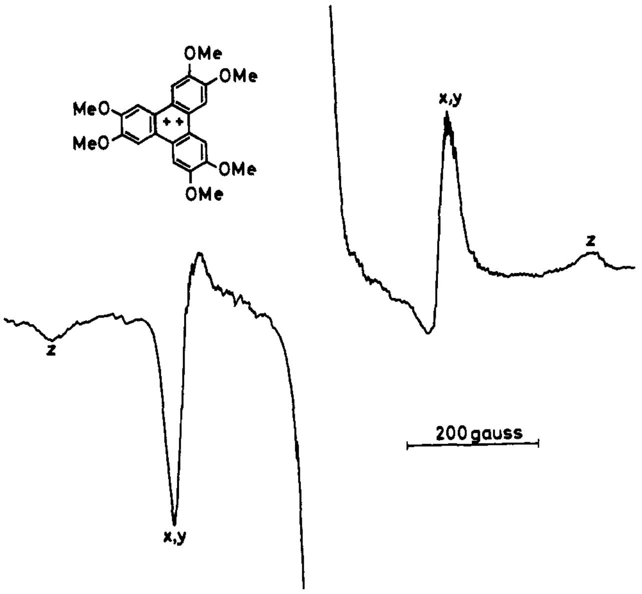


Figure 2. High-field ($\Delta m_s = 1$) esr spectrum of **2**. The central line is due to the monocation.

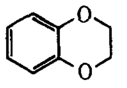
HMT was oxidized to **1** in TFA and the solution then diluted with an equal volume of $HFSO_3$, the room temperature cyclic voltammogram indicated that **2** undergoes further irreversible oxidation. On cooling the solution to −70°, the reversible oxidation of **2** to **3** was observed (Figure 1c). 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



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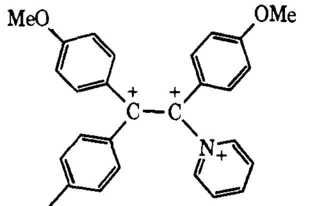
examples recently reported are the trimerization of anthracene[6] and mesitylene.[7]

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



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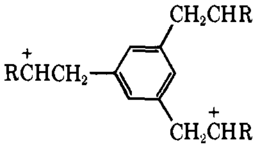

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reported. Our application of low-temperature voltammetry to observe **3** illustrates the usefulness of this technique in the observation of unstable intermediates and it is indeed surprising that this technique has so seldomly been used. We are continuing our studies in related systems in an attempt to observe other triplet dications.

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[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).

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(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.

on the above system in the conventional manner using photon counting. For the circular dichroism measurements the plane polarized laser beam was passed through a potassium dideuterium phosphate electrooptical modulator before being focused on the sample. The electrooptical modulator was driven by the amplified 500-Hz internal oscillator signal of a lock-in amplifier. The amplitude of the ac voltage applied to the electrooptical modulator was set at the "quarter-wave potential" corresponding to the laser wavelength, 4880 Å. The light illuminating the sample therefore alternated between right and left circularly polarized 500 times a second. This arrangement generates three main signals at the output of the photomultiplyer tube: (a) a dc component proportional to the sum of the Raman intensities due to right and left circularly polarized incident light (the normal Raman effect); (b) a 1000-Hz component, the amplitude of which depends on both the intensity and the depolarization ratio of the Raman line; and (c) a 500-Hz component proportional to the difference in the Raman intensities with right and left circularly polarized light incident on the sample, as well as higher harmonics. The lock-in amplifier rejects all components of the composite output signal except that at 500 Hz which is in phase with the signal impressed upon the electrooptical modulator and, hence, will display directly the difference in Raman intensity for right and left circularly polarized light incident on the sample. The phase sensitivity of the amplifier will, moreover, indicate the sign of the difference between the scattered intensities due to right and left circularly polarized light, that is, the sign of the Raman circular dichroism.

The Raman circular dichroism may be expressed in two ways, either as the observed quantity $I_r - I_l$, where I_r and I_l are the intensities of the scattered light with right and left circularly polarized incident light respectively, or preferably as a normalized dimensionless quantity Δ,[2,4] where

$$\Delta = (I_r - I_l)/(I_r + I_l)$$

This latter quantity which is similar to the "dissymmetry factor," g, in electronic circular dichroism, can be defined for both parallel, $\Delta_{\|}$, and perpendicular, $\Delta_{\perp}$, polarization.

In Figure 1 we show the normal Raman spectrum in both polarizations and the Raman circular dichroism spectra for α-phenylethylamine in the (±), (+), and (−) forms of the pure liquids in parallel polarization. In addition, we give an approximate normalized spectrum, $\Delta_{\|}$, measured by dividing the peak heights of the circular dichroism spectrum by the normal Raman spectrum in parallel polarization. [Δ can be measured directly by (electronically) combining the dc and ac signals.] In perpendicular polarization the Raman circular dichroism is at least 100 times weaker and was barely detectable even in the strongest line. As may have been expected and was theoretically predicted,[2,4] the Rayleigh line, anti-Stokes lines, and the Stokes lines all show Raman circular dichroism, and the corresponding lines in the anti-Stokes and Stokes regions have the same sign. Two arresting features are also observed; every line in all regions of the spectrum has the same sign for a given enantiomer and those lines which are more strongly polarized are also those which show the stronger Raman circular dichroism. We have found this to be true for five other compounds where we have observed the effect, α-phenylethylamine showing the strongest effect. All these molecules, however, were devoid of any symmetry elements and formally all the transitions belonged to the totally symmetric representation. It may turn out that dissymmetric molecules of higher symmetry will show Raman circular dichroism of opposing sign within the same spectrum. Whatever the case, the possible use of this technique in the assignment of vibrational spectra and its application to the designation of the absolute configurations and structures of large and small molecules presents an exciting prospect.

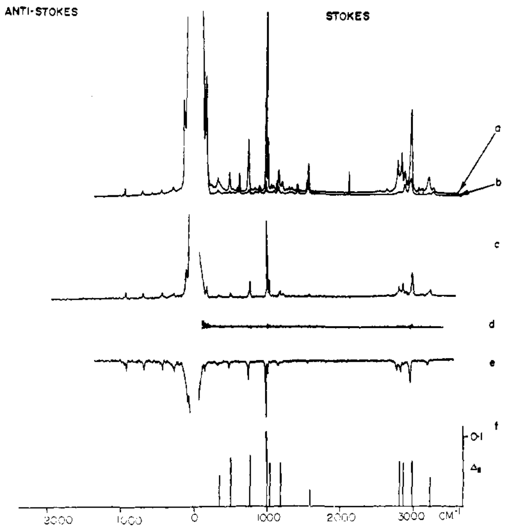

Figure 1. The spectra are as follows: (a) the normal Raman spectrum in parallel polarization of α-phenylethylamine, (b) the normal Raman spectrum of the same molecule in perpendicular polarization, (c) the Raman circular dichroism spectrum of (−)-α-phenylethylamine in parallel polarization, (d) the Raman circular dichroism of (±)-α-phenylethylamine in parallel polarization, (e) the Raman circular dichroism of (+)-α-phenylethylamine in parallel polarization, and (f) the normalized Raman circular dichlorism, Δ, in parallel polarization for (−)-α-phenylethylamine. Note: lines undermarked by dots in (a) are due to fluorescent room illumination.

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The Energy Barrier to Racemization in a *vic*-Dialkylidenecycloalkane Analog. 3,4-Diisopropylidene-8-phenyl-1,6,8-triazabicyclo-[4.3.0]nonane-7,9-dione

Sir:

A type of molecular dissymmetry which appears so far to have escaped quantitative study is that shown by appropriately substituted *vic*-dialkylidenecycloalkanes

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(4) L. D. Barron, *J. Chem. Soc. A*, 2889 (1971).