The circular dichroism spectra of I, previously described, are reported. Figure 1 gives the absorption spectrum of the *cis* complexes (I) (A), and the circular dichroism spectra of the ethylene complex (B), the pure *cis*-2-butene complex (C), the (+) (D) and (−) (E) diastereoisomers of the propylene complex, the equilibrium mixture of the diastereoisomers (F), and the pure (−) diastereoisomer (G) of the *trans*-2-butene complex. The curves show that the ethylene and the *cis*-2-butene complexes, which cannot form the diastereoisomers III and IV, give little or no circular dichroism in the region of the lowest energy d → d electronic transition of platinum(II) at 27,000 $\text{cm}^{-1}$, whereas the (+) and (−) diastereoisomers of the propylene complex give, respectively, a positive and a negative circular dichroism band in that region. The magnitude of the dichroism $(\epsilon_l - \epsilon_r)_{\max}$ is nearly the same for the two diastereoisomers. In general, the circular dichroism of the lowest energy d → d electronic excitation of transition metal complexes has been found[3] to be particularly sensitive to the absolute stereochemistry of the complex.

These observations suggest that the configuration of the olefin relative to the metal and the other ligands is reflected in the sign of the circular dichroism band near 27,000 $\text{cm}^{-1}$ and that the composition of a mixture of diastereoisomers is given semiquantitatively by the magnitude of that dichroism. The comparison of the sign and the magnitude of the lowest energy circular dichroism band given by the equilibrium mixture of the diastereoisomers of the *cis* complex derived from *trans*-2-butene (Figure 1, F) with that of the corresponding pure (−) diastereoisomer (Figure 1, G) suggests that the latter predominates in the equilibrium mixture to the extent of 40% in ethanol solution at room temperature.

These inferences are unambiguously supported by the exchange reaction of the ethylene complex (I) with racemic *trans*-cyclooctene. This complex was allowed to react at room temperature with 2 moles of (*R*,*S*)-*trans*-cyclooctene in methylene chloride or acetone solution until complete exchange.

The excess olefin was then removed *in vacuo* at 10°, leaving as an oil the crude mixture of the diastereoisomers of the *trans*-cyclooctene complex (I).

*Anal.* Calcd for $C_{16}H_{23}Cl_2NPt$: C, 38.62; H, 5.06; Pt, 39.27. Found: C, 39.03; H, 4.89; Pt, 38.71.

The unreacted olefin was the (−) olefin with enantiomeric purity of about 30%. The treatment of the crude mixture (a solid after washing with petroleum ether and extensive pumping) of diastereoisomers with KCN in ethylene glycol–methanol yielded the (+) olefin with the same degree of optical purity.

Further work is in progress to check the above interpretation of the optical rotation data by means of CD measurements on a more extended range of olefin complexes (I).

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## Oxidation, Reduction, and Electrochemiluminescence of Aryl-Substituted Isobenzofurans and Isoindoles

*Sir:*

Recent investigations have shown[1-6] that a number of fluorescent aromatic hydrocarbons luminesce in conducting aprotic media under an applied ac voltage. We wish to report that certain heterocyclic compounds also luminesce or electrochemiluminesce (ECL) under these conditions. Because some of these heterocyclics ECL brightly, they have been used in studies designed to provide mechanistic information regarding the ECL process. The latter will be reported in a separate paper. We report here only on the ECL and related properties of 1,3,4,7-tetraphenylisobenzofuran[7] (I) and on the effect of structural modifications on these properties.

The cell used in these studies consisted of two 1-$\text{cm}^2$ 80-mesh platinum gauze electrodes spaced 2 mm apart in a 15-ml glass container. The fluorescer was examined in a conducting medium consisting of 0.1 *M* tetra-*n*-butylammonium perchlorate in dry, deaerated N,N-dimethylformamide (DMF). Upon imposing 8 v peak to peak (60 cps) with a square wave generator on this solution,[8] the intensity of light emitted from the region of the electrodes[9] increased from 1.9 ft-lamberts to 20 ft-lamberts (*cf.* Figure 1) as the concentration of I was increased from 1 m*M* to almost 6 m*M* (saturated). The intensity of the ECL emission of the saturated solution remained at or above 18 ft-lamberts in the 50–3000-cps range with a maximum of 22 ft-lamberts being measured at 120–130 cps.

Compound I exhibits an intense green fluorescence in DMF solution (fluorescence efficiency [Φ] = 0.51) with a maximum at 530 mμ. The ECL emission is *identical* spectrally with the fluorescence emission. Oxidation (rotating platinum electrode) and reduction (dropping mercury electrode) of I in DMF occurs by one-electron changes at $E_{1/2} = +0.98$ and $-1.86$ v *vs.* sce, respectively. A second one-electron reduction wave presumably due to dianion formation can be seen at $E_{1/2} = -2.11$ v and a third wave at $E_{1/2} = -2.38$ v can also be detected. Cyclic voltammetry in the same solvent shows that the first reduction product is stable (lifetime > 15 sec), while the first oxidation product and the second reduction products are both unstable under these conditions. By varying the voltage scan rate lifetimes of 1 sec are indicated for both the cation and dianion.

Substitution of the *para* positions of the phenyl substituents on the furan ring with methoxy groups to give

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(1) Technical Report No. 4 to the Office of Naval Research and Advanced Research Projects Agency, Contract Nonr 4200(00), July 1964.

(2) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(3) R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964).

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(5) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **87**, 139 (1965).

(6) E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).

(7) E. D. Bergmann, S. Blumberg, P. Brasha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

(8) Square wave input was provided by a 2 Trygon Electronics HR20-5A DC power supply and a transistorized switch which alternated between the positive and negative outputs of the two power supplies at 60 cps.

(9) Brightness measurements were obtained with a Photo Research Corporation Model UB 1/2 spectral brightness meter which could be focused on the cell electrodes.

1,3-bis-*p*-anisyl-4,7-diphenylisobenzofuran (II),[10] mp 226°, failed to improve the stability of the cation radical (lifetime estimated from cyclic voltammetry 0.6 sec). This compound had considerably enhanced solubility over that of I and the position of its fluorescence maximum was shifted to 568 m$\mu$, without significant change in fluorescence efficiency ($\Phi = 0.53$). The intensity of ECL emission for II was also studied as a function of fluorescer concentration as seen in Figure 1. With all other variables held constant, maximum ECL emission intensity was found at the 10 m*M* fluorescer concentration level (37 ft-lamberts) with 7 v applied to the electrodes. At both lower and higher concentrations of II the ECL brightness diminished. *p*-Phenyl substituents on the furan phenyl groups of I to give 1,3-di-*p*-biphenyl-4,7-diphenylisobenzofuran (III),[10] mp 240–241°, also resulted in a bathochromic shift of the fluorescence maximum, $\lambda_{\max}^{\mathrm{Fl}}$ 540 m$\mu$, $\Phi = 0.57$, but decreased solubility (~2 m*M*) resulted in diminished ECL intensity. *p*-Methoxy substitution on the phenyl substituents of the benzo ring of I leads to a hypsochromic shift of the fluorescence maximum and a decreased fluorescence efficiency and ECL intensity. Thus, in contrast to II, 1,3,4,7-tetra-*p*-anisylisobenzofuran (IV),[10] mp 233–235°, had $\lambda_{\max}^{\mathrm{Fl}}$ 547 m$\mu$ and $\Phi = 0.49$, while 1,3-diphenyl-4,7-di-*p*-anisylisobenzofuran (V),[10] mp 195–196°, had $\lambda_{\max}^{\mathrm{Fl}}$ 515 m$\mu$ and $\Phi = 0.33$.

Cyclic voltammograms of the solutions of these compounds showed that their monoanions all had stabilities >15 sec while the stabilities of their monocations were in the range 0.5–4 sec.

No difference could be detected between the ECL emission spectra of these compounds and their fluorescence spectra. The fluorescence spectra were corrected by computer analysis for the nonlinear wavelength response of the phototube in the 500–600-m$\mu$ region.

A number of known related compounds were investigated. These include 1,3-diphenylisobenzofuran, 1,3,-4,5,6,7-hexaphenylisobenzofuran, and 1,3,4,7-tetraphenylisobenzothiophene. These also electrochemiluminesced but with considerably lower intensity than the previously described compounds.

N-Methyl-1,3,4,7-tetraphenylisoindole (VI),[10,11] mp 281–283°, and N-methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole (VII),[10,11] mp 237–239°, are also strong fluorescers ($\Phi = 0.53$ and 0.52) in DMF solution and their electrochemiluminescent emission is also identical with their fluorescence emission with maxima at 490 and 507 m$\mu$, respectively. Cyclic voltammetry shows that contrary to the isobenzofurans, these compounds form stable cation radicals (>15 sec lifetimes) and unstable (1–2-sec lifetimes) anions. Diffusion current measurements indicate that the reduction of these isoindoles involves two electron uptake, while oxidation involves one-electron transfer.

It is desirable to study the ECL process with fluorescent materials which are stable in both oxidized and reduced forms. Although the compounds described here approach this condition they do not reach it. It is apparent, however, that fluorescent quinoidal compounds such as these offer maximized opportunities for such stabilization and further synthetic efforts along these lines are being made.

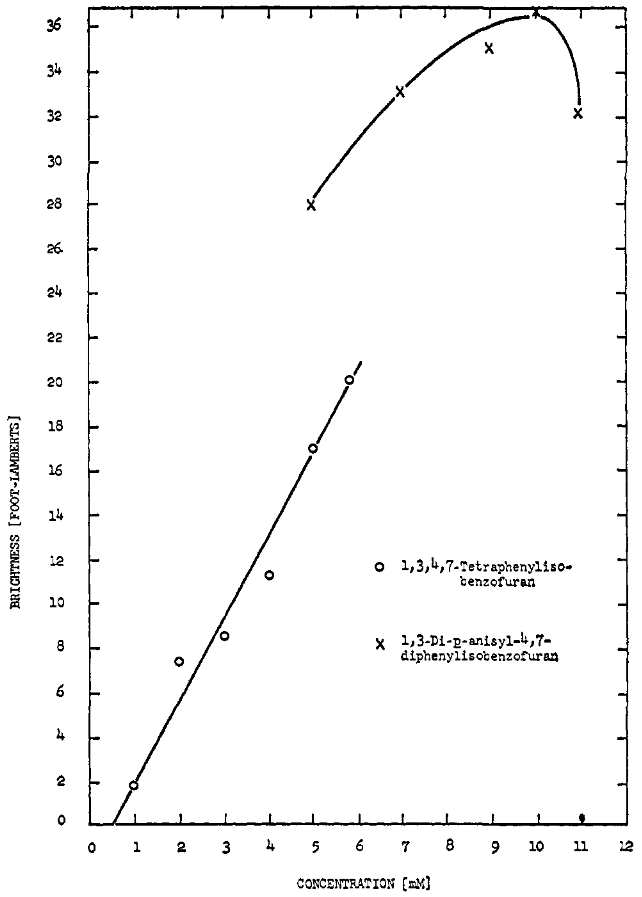

Figure 1. Effect of fluorescer concentration on ECL brightness.

LCAO–MO calculations indicate that the coefficients of the wave function of the highest filled molecular orbital of the isobenzofuran system are very large at the 1,3 positions, while the lowest unfilled molecular orbital of this system has coefficients of about the same value for the 1,3 and 4,7 positions. The observed shifts in emission maxima on *p*-methoxy substitution can be rationalized on this basis since perturbation theory predicts that donor substituents will raise the energy of the molecular orbitals to an extent which is proportional to the coefficient of the molecular orbital of the base molecule at the position of the substituent. Similarly, the calculations correctly predict the hypsochromic shift in maxima in going from the isobenzofuran to the isoindole series. The wave function of the highest filled molecular orbitals of these molecules has a node through the heteroatom while the lowest unfilled molecular orbitals do not. Nitrogen, being the less electronegative electron-pair donor, raises the energy of the lowest unfilled molecular orbital more than oxygen resulting in a greater transition energy.

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[10] All new compounds described had satisfactory elemental analyses.

[11] Prepared by a modification of the general procedure described by J. C. Emmett, D. F. Veber, and W. Lwowski, *Chem. Commun.*, 272 (1965).