nitrate salt present for substitution on the side chain rather than on the ring. This is, *per se*, almost compelling evidence for a mechanism including a step in which a radical abstracts a hydrogen atom from the aromatic substrate, and, in fact, all of the observed products can be conveniently rationalized from this point of departure.[11]

(11) For a similar interpretation of the anodic methoxylation of alkylbenzenes, see, K. Sasaki, H. Urata, K. Uneyama, and S. Nagaura, *Electrochim. Acta*, 12, 137 (1967).

Electrochemiluminescence of Aryl-Substituted Isobenzofurans, Isoindoles, and Related Substances[1]

Arnold Zweig, Gerlinde Metzler, Arthur Maurer, and Bernard G. Roberts

Contribution from the American Cyanamid Company,
Chemical and Research Service Departments, Central Research Division,
Stamford, Connecticut 06904. *Received March 1, 1967*

Abstract: The electrochemiluminescence emission, polarographic half-wave oxidation and reduction potentials, anion- and cation-radical stabilities, fluorescence spectra, and fluorescence efficiencies of a number of aryl-substituted isobenzofurans, isoindoles, and similar compounds have been examined in N,N-dimethylformamide solution. These data, together with molecular orbital calculations, permit several types of structure–property comparisons to be made which provide insight into the factors which affect ion-radical stability and electrochemiluminescence.

Electrochemiluminescence (ecl) may be defined as a process in which molecules capable of luminescing are raised to an excited electronic state by electrochemical energy. Of those *fluorescent* aromatic hydrocarbons which luminesce on successive electrochemical oxidation and reduction steps at platinum electrodes in polar aprotic media, rubrene (5,6,11,12-tetraphenyltetracene) has been found to emit the brightest visible light for the longest period.[2,3] The duration of this electrochemiluminescence under standardized conditions (*cf.* Experimental Section) is at best a matter of hours, and at the end of the emission period the fluorescer is found to be consumed. Purification of the components of the system and rigorous exclusion of air and moisture afford some small improvement in the brightness-duration characteristics; however, it is apparent that some factor intrinsic to the ecl process remains responsible for the consumption of material. The electrochemical processes at the electrodes produce ion radicals and these must be involved in the eventual production of excited singlets. The ion radicals and the excited state of the molecule are thus implicated as possible sources for degradation of the fluorescer. Attempted photolysis of several highly fluorescent and electrochemiluminescent molecules showed them to be quite photostable in the absence of oxygen.[4] Investigation of the contents of an exhausted rubrene ecl cell showed the presence of pseudorubrene,[5] a compound which had been previously reported as being formed on acid treatment of rubrene.[6] Since the cation radical of rubrene is known to be unstable in the solvent employed, N,N-dimethylformamide,[2,3] it appears that rearrangement of the rubrene cation to a pseudorubrene cation competes with the process leading to emission.

The report by Bergmann and co-workers[7] that 1,4,5,8-tetraphenylnaphthalene is a fluorescent compound which does not undergo rearrangement under the acid conditions which are responsible for the rubrene rearrangement prompted us to repeat their preparation of this compound. The synthesis involves Diels–Alder condensation of 1,4-diphenyl-1,3-butadiene with 1,2-dibenzoylethylene, aromatization of the cyclohexene adduct, and ring closure of the resulting *o*-diaroylbenzene to 1,3,4,7-tetraphenylisobenzofuran. Diels–Alder reaction of the isobenzofuran with acrolein, followed by treatment of the adduct with anhydrous hydrochloric acid, led to 1,4,5,8-tetraphenylnaphthalene-2-carboxaldehyde which was readily decarbonylated to produce the desired hydrocarbon. The latter is indeed a good electrochemiluminescent compound with a considerably longer ecl emission lifetime than rubrene under comparable conditions. Its ecl properties have previously been reported.[8] It was found that an intermediate in this synthesis, 1,3,4,7-tetraphenylisobenzofuran, an intensely green fluorescer, electrochemiluminesced with a brightness which was orders of magnitude greater than that of the hydrocarbons under the same conditions. Furthermore, the emission from the isobenzofuran endured for longer periods under comparable conditions. This finding resulted in an investigation of the chemical and physical variables involved in the ecl emission from isobenzofurans and related substances. In this paper we report on the effects of variation of fluorescer structure on the emission and

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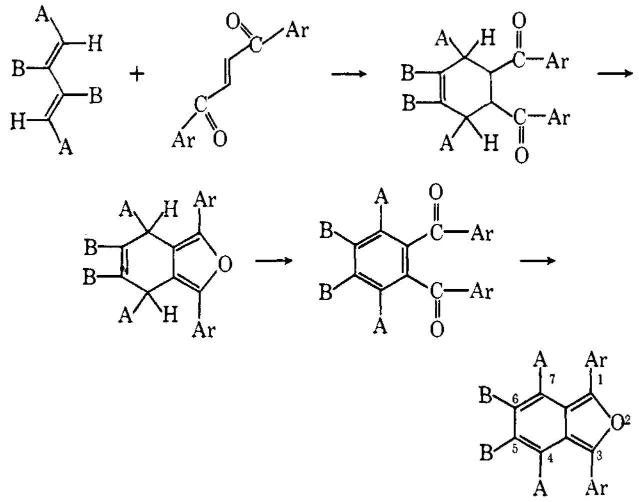
(1) A preliminary account of part of this work has been published: A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, 88, 2864 (1966).
(2) D. L. Maricle and A. Maurer, *ibid.*, 89, 188 (1967).
(3) M. M. Rauhut, D. L. Maricle, *et al.*, Technical Reports No. 4 and 5 to the Office of Naval Research and Advanced Research Projects Agency, Contract Nonr 4200(00), July 1964, AD 602,272, AD 606,989.
(4) A. Zweig, unpublished observations.
(5) D. L. Maricle and A. H. Maurer, unpublished observations.
(6) C. Moureu, C. Dufraisse, and G. Berchet, *Compt. Rend.*, 185, 1085 (1927); C. Moureu, C. Dufraisse, and L. Enderlin, *ibid.*, 188, 673 (1929); C. Dufraisse and G. Amiard, *ibid.*, 220, 695 (1945).
(7) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, 20, 195 (1964).
(8) A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, 32, 1322 (1967).

on related molecular electrochemical and spectroscopic properties. These studies have enabled us to probe the mechanism of the ecl process in greatest depth on the more efficient compounds. The results of the mechanism studies will be reported separately.

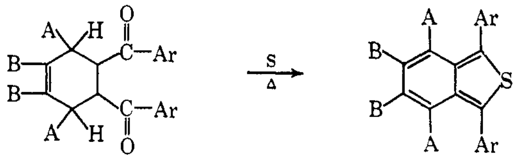
Preparation of Compounds

Adams and Gold[9] found that Diels–Alder condensation of 1,3-butadienes with diaroylethylenes gave the corresponding diaroylcyclohexenes. The cyclohexenes were readily converted to dihydroisobenzofurans and then into *o*-diaroylbenzenes. The latter were converted into the highly fluorescent isobenzofurans as shown in Chart I. These workers also noted that the isobenzofurans were good dienes in the Diels–Alder reaction and that their adducts with maleic anhydride could be converted to naphthalene derivatives. The synthesis of the unsubstituted bis(*peri*-tetraphenylnaphthalene), however, remained to be reported by Bergmann, *et al.*[7] (*vide supra*), and also by Dufraisse and Lepage.[10] The latter workers used acrylic acid as the dienophile in otherwise similar reaction scheme. The synthesis of 1,4,5,8-tetraphenylnaphthalene is of special interest because the phenyl and naphthyl portions of the molecule have perpendicular nodal planes. Simple molecular orbital theory predicts no interaction of perpendicular systems; however, studies of the *peri*-substituted phenylnaphthacenes indicate that the phenyls may exert a considerable bathochromic effect on the naphthacene absorption bands.[11]

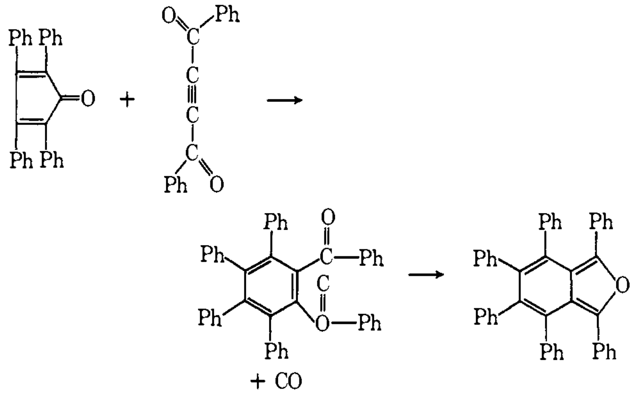
Chart I



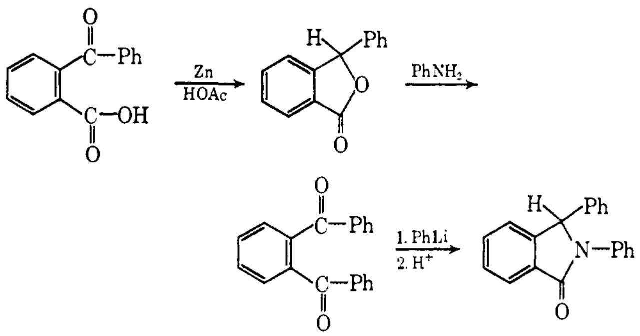
Further chemical and spectroscopic studies of aryl-substituted isobenzofurans were reported by Allen and Gates.[12] These workers reported several new derivatives of 2,3-disubstituted 1,3-butadienes. They also found that heating the diaroylcyclohexenes with sulfur resulted in the formation of the corresponding isobenzothiophenes.



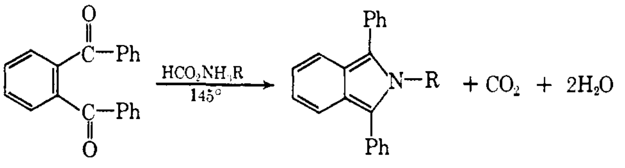
Reid and Bönnighausen[13] conducted extensive studies on the preparation and chemistry of isobenzofuran systems and described 1,3,4,7-tetraphenylisobenzofuran and 1,3,4,5,6,7-hexaphenylisobenzofuran. The latter was prepared by the reaction of dibenzoylacetylene with tetraphenylcyclopentadienone to give the fully aromatic *ortho* diketone which underwent ring closure in the normal manner.



The aryl-substituted isoindoles,[14,15] electronically very similar to the isobenzofurans, are also fluorescent. Until very recently, few references to isoindoles could be found in the literature. Theilacker and Schmidt[14] described the preparation of 1,2,3-trisubstituted isoindoles employing *o*-benzoylbenzoic acid in a multistep synthesis as indicated here for the 1,2,3-triphenyl derivative.



Emmett, Veber, and Lwowski[15] found that *o*-dibenzoylbenzene reacts with ammonium formate and N-substituted ammonium formates to give isoindoles in one step, under Leuckart reaction conditions.



R=H or CH_3

We have repeated the preparations of 1,3-diphenyl-, 1,3,4,7- and 1,3,5,6-tetraphenyl-, and 1,3,4,5,6,7-tetraphenylisobenzofurans, 1,3,4,5-tetraphenylisobenzothio-

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(9) R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 56, 2038 (1940); R. Adams, U. S. Patent 2,356,907 (1954).

(10) C. Dufraisse and Y. Lepage, *Compt. Rend.*, **258**, 1507 (1964).

(11) H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

(12) C. F. H. Allen and J. W. Gates, Jr., *ibid.*, **65**, 1283 (1943).

(13) W. Ried and K. H. Bönnighausen, *Ann.*, **639**, 61 (1960).

(14) W. Theilacker and W. Schmidt, *ibid.*, **597**, 95 (1955); **605**, 43 (1957).

(15) J. C. Emmett, D. F. Veber, and W. Lwowski, *Chem. Commun.*, 272 (1965); J. C. Emmett and W. Lwowski, *Tetrahedron*, **22**, 1011 (1966).

Table I. Electrochemiluminescent Substances. Absorption and Emission Data in DMF Solution

	λ_1	Log ϵ	λ_2	Log ϵ	λ_3	Log ϵ	λ_{max} fluorescence and ecl	Φ	Rel ecl intensity
1,3-Diphenylisobenzofuran	415	4.45	310	3.95	275	4.5	486	...	0.04
1,3,4,7-Tetraphenylisobenzofuran	404	4.08	325	3.66			530	0.50	20
1,3,5,6-Tetraphenylisobenzofuran	450 s	4.17	428	4.29	333	4.06	492	0.84	0.2
1,3,4,5,6,7-Hexaphenylisobenzofuran	399[a]	4.12	285 s	4.35	273	4.37	503[a]	0.64[a]	...[b]
1,3-Di-*p*-biphenylyl-4,7-diphenylisobenzofuran	404	4.13	285 s	4.33			540	0.57	17[d]
1,3,4-Triphenyl-7-(9-anthracenyl)isobenzofuran	415 s	4.12	390	4.27	370	4.18	530	0.23	...[c]
1,3-Di-*p*-anisyl-4,7-diphenylisobenzofuran	415	4.18	320 s	3.95	275 s	4.26	568	0.53	37
1,3-Diphenyl-4,7-di-*p*-anisylisobenzofuran	420	4.38	350 s	3.91			515	0.33	32
1,3,4,7-Tetra-*p*-anisylisobenzofuran	412	4.24	325 s	3.96			547	0.49	19
N-Methyl-1,3-diphenylisoindole	377	4.27	332	4.01	276	4.20	453	0.73	...[c]
N-Methyl-1,3,4,7-tetraphenylisoindole	384	3.53	328 s		298 s		490	0.53	3.8
N-Methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole	386	3.75	325 s	3.59			507	0.52	7.2
1,2,3-Triphenylisoindole	375	4.07	327	3.88	315 s	3.85	448	0.11	...[c]
1,3,4,7-Tetraphenylisobenzothiophene	390	3.81	265 s	3.03			523	0.24	...[c]

[a] Measured in methylcyclohexane. [b] Not measured. [c] Too dim to measure accurately. [d] 2 m*M* fluorescer concentration.

phene, and 1,2,3-triphenyl- and 1,3-diphenyl-2-methylisoindole. Suitable modifications of the literature procedures were adopted to prepare the various substituted derivatives of these *o*-benzoquinoidal compounds which are listed in the tables. The reaction conditions described in the literature were not generally applicable and many syntheses required adjustment of reaction variables before useful yields of the desired materials were obtained. These details are described in the Experimental Section.

Electrochemiluminescence and Spectral Properties. The ecl emission was initially examined in N,N-dimethylformamide (DMF) solutions which were 2–10 m*M* in the electroactive substance and 0.1 *M* in tetra-*n*-butylammonium perchlorate electrolyte. The dry, deaerated solution contained a pair of closely spaced (*ca.* 1 mm) parallel platinum gauze electrodes. The cells could be sealed on a vacuum line, tightly stoppered after filling in a drybox, or continuously bubbled with argon with little variation in initial emission properties, as long as oxygen and moisture were excluded. On application of alternating current (generally 6–8 v) of appropriate frequency, employing a square-wave voltage generator, luminescence was seen at the electrodes. Applied voltages of this magnitude are required because of the appreciable *iR* drop in this aprotic solvent. The emission from these systems may be classified in two broad categories: (1) those that are identical with normal fluorescence emission and (2) those which are spectrally much different from the fluorescence emission. All of the emissions from the compounds reported in this study fall into the first category. Within this group qualitative distinction can be made with regard to the ecl emission brightness. In the cells employed, some of the systems emitted light of sufficient brightness to be clearly discernible in a lighted room, while the emission from others, even under optimum conditions, could be detected only in a dark room, and in some instances eye adaption to the dark was needed. Except for the dimmest emissions, relative brightness could be measured by a foot-lambert meter which has a spectral response similar to that of the eye. The spectral distribution of the ecl and fluorescence emissions were obtained by placing the operating cell in a calibrated radiometer–fluorimeter (*cf.* Experimental Section).

The brightness measurements reported in Table I were all made with a 5 m*M* concentration of fluorescer, solubility permitting, using as close to identical conditions as possible. The maximum light intensity was measured within 1 min of the time the power was turned on. The emission intensity was affected by the applied voltage with the maximum intensity occurring in the 6–8-v (applied) range. The initial brightness measurements at the voltage which gave maximum brightness was found to be reproducible to ±10% as long as the voltage settings were unchanged. Semiquantitative emission duration studies were made as a function of the applied voltage. Decreasing the voltage below that required for maximum initial brightness increased the lifetime of detectable emission but the intensity integrated over the time emission could be detected decreases sharply if the voltage was dropped as much as 2.

The absorption and fluorescence spectral maxima for the compounds studied are also reported in Table I. The extinction coefficients at the absorption maxima are reported, as are the fluorescence emission maxima which are corrected for the nonlinear wavelength response of the phototube. Also reported in Table I are the quantum efficiencies of fluorescence obtained on irradiation of DMF solutions of these compounds with a calibrated light source.

Cyclic Voltammetry. Cyclic voltammograms were obtained for the compounds listed in Table II. The current–voltage curves were obtained under the same conditions as used for electrochemiluminescence studies. The solutions were examined at a platinum electrode employing a variable voltage scan rate. Figure 1 shows the cyclic voltammogram for 1,3,4,7-tetraphenylisobenzofuran at a scan rate of 5 v/10 sec. The metastable cation of this isobenzofuran shows a continuingly decreasing rereduction wave as the scan rate is decreased. The dianion shows almost identical behavior. The monoion radical lifetimes reported in Table II are calculated from the slowest cyclic voltammogram scan rate at which the rereduction of the cation, or reoxidation of the anion, is *detectable*. This value provides a measure of the relative stabilities of the ion radicals under ecl conditions.

The oxidation and reduction potentials reported in Table II are "peak potentials" which are related to the

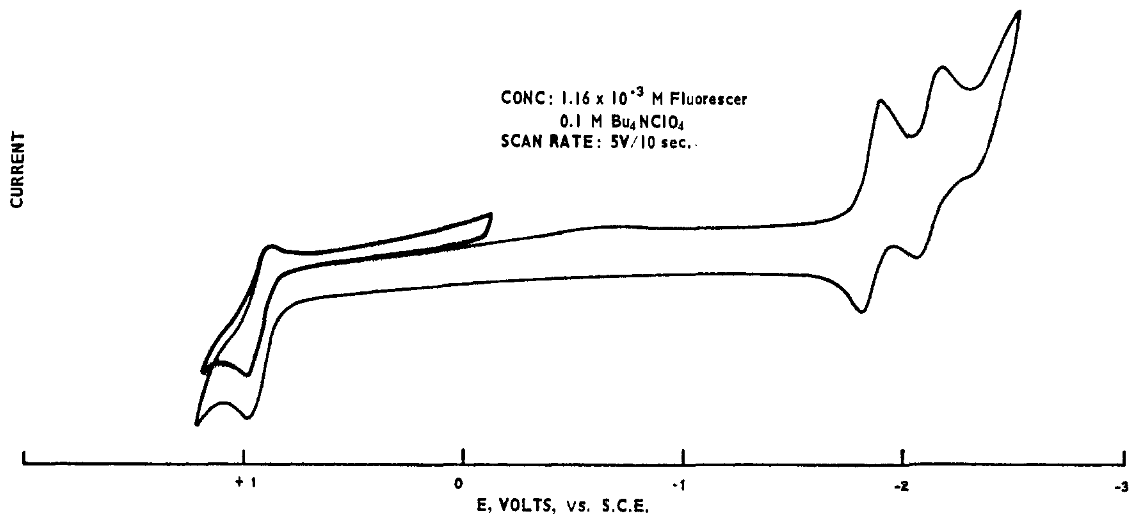

Figure 1. Cyclic voltammogram of 1,3,4,7-tetraphenylisobenzofuran in N,N-dimethylformamide.

normal half-wave potentials[16] by the expressions

$$E_{pk}^{\text{oxidn}} = E_{1/2} + 1.1\,\frac{RT}{nF}$$

$$E_{pk}^{\text{redn}} = E_{1/2} - 1.1\,\frac{RT}{nF}$$

Polarographic reduction curves for most of the isobenzofurans were also run at a dropping mercury electrode and the measured diffusion currents were consistent with a one-electron transfer process. Since the cyclic voltammograms showed first oxidation and reduction peak heights to be nearly the same, we infer that the oxidation process also involves one-electron transfer.

Table II. Peak Potentials and Estimated Lifetimes of Ion Radicals of Isobenzofurans

	E^{oxidn}, v	Lifetime, sec	E^{redn}, v	Lifetime, sec
1,3-Diphenylisobenzofuran	+0.79	<0.1	−1.92	>20
1,3,4,7-Tetraphenylisobenzofuran	0.98	1	−1.90	>20
1,3,5,6-Tetraphenylisobenzofuran	0.85	<0.01	−1.79	>20
1,3,4,5,6,7-Hexaphenylisobenzofuran	0.95	<0.01	−1.98	>20
1,3-Di-*p*-biphenylyl-4,7-diphenylisobenzofuran	0.94	5	−1.78	>20
1,3,4-Triphenyl-7-(9-anthracenyl)isobenzofuran	0.93	1	−1.86	>20
1,3-Di-*p*-anisyl-4,7-diphenylisobenzofuran	0.76	0.6	−2.00	>20
1,3-Diphenyl-4,7-di-*p*-anisylisobenzofuran	0.91	4	−1.96	>20
1,3,4,7-Tetra-*p*-anisylisobenzofuran	0.74	0.5	−2.09	>20
N-Methyl-1,3-diphenylisoindole	0.69	>20	−2.40	<0.1
N-Methyl-1,3,4,7-tetraphenylisoindole	0.72	>20	−2.45	2
N-Methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole	0.60	>20	−2.54	1–2
1,2,3-Triphenylisoindole	0.76	>20	−2.30	<0.03
1,3,4,7-Tetraphenylisobenzothiophene	>1.0	...	−1.85	5

The cyclic voltammograms of the N-methylisoindoles all showed a reduction wave of approximately twice the height of their oxidation waves. Conventional polarography confirmed that reduction of these species involved two-electron transfer. Thus, for example, N-methyl-1,3,4,7-tetraphenylisoindole has a half-wave reduction potential of −2.35 v relative to sce at a dropping mercury electrode in DMF. Its I_d is 3.08, quite characteristic of a two-electron transfer process.

The cyclic voltammograms indicated some anionic reoxidation. Two explanations are possible. Either the second electron uptake is incomplete, so that a small amount of radical anion is present which is subsequently reoxidized, or the dianion itself, like the isobenzofuran dianion, has sufficient stability to be reoxidized. From the data at hand we are unable to differentiate between these possibilities.

2,5-Diarylfurans. The emission spectroscopy, electrochemistry, and ecl emission of 2,5-diphenyl- and 2,5-di-*p*-anisylfuran were briefly examined as part of the survey of compounds related to the isobenzofurans. 2,5-Diphenylfuran has previously been reported to be fluorescent[17] (blue-violet). We have found $\lambda_{\text{max}}^{\text{fluor}}$ for 2,5-di-*p*-anisylfuran to be 385 mμ. Cyclic voltammetry showed that the anion of 2,5-diphenylfuran formed at −2.45 v (peak) in DMF has a lifetime of 0.5 sec, while the cation (E_{peak} = +1.29 v) has a detectable lifetime of only 0.03 sec.

2,5-Di-*p*-anisylfuran reduces ($E_{1/2}$ = −2.60 v) to form an anion with a lifetime of 0.5 sec and oxidizes at E_{peak} = +0.95 v to form a cation with lifetime of 0.2 sec. When 8 v was applied to a 5 m*M* solution of

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(16) H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).

(17) S. M. King, C. R. Bauer, and R. E. Lutz, *J. Am. Chem. Soc.* 73, 2253 (1951).

Table III. Spectroscopic Properties in DMF. 1,4-Diaryl-1,3-butadienes, RCH═CHCH═CHR′

		Absorption maxima, mμ							
R	R′	λ_1	Log ϵ	λ_2	Log ϵ	λ_3	Log ϵ	$\lambda_{max}^{fluor.}$	Φ
C_6H_5	*p*-CNC_6H_4	380	4.30	359	4.57	346	4.56	405	0.15
C_6H_5	α-$C_{10}H_7$	367 s	4.58	349	4.54	333 s	4.59	420	0.21
C_6H_5	9-Anthracenyl	400	4.17	325	4.25	311	4.22	538	0.23
C_6H_5	10-Methoxy-9-anthracenyl	408	4.19	328	4.29	314	4.26	560	0.007
p-$C_6H_5C_6H_4$	*p*-$C_6H_5C_6H_4$	387 s	4.51	366	4.70	352	4.63	428	0.84
α-$C_{10}H_7$	α-$C_{10}H_7$	362	4.51	298 s	3.87	272 s	3.98	462	0.44

2,5-di-*p*-anisylfuran under the previously described ecl conditions, a blue emission just measurable on the light detection meter (0.03 foot-lambert), which lasted several minutes, was observed. It is apparent from these results that simple furans are less satisfactory than isobenzofuran derivatives for study of the ecl emission phenomenon.

1,4-Diarylbutadiene Intermediates. For the preparation of new isobenzofurans a number of 1,4-diarylbutadienes had to be prepared. One of these, 1-phenyl-4-(9-anthracenyl)-1,3-butadiene, appeared to be a fairly bright yellow fluorescer[18] (λ_{max}^{fluor} 540 mμ, $\Phi = 0.22$) in DMF. Since the electrochemiluminescence of the isobenzofurans was discovered incidental to another investigation, it seemed necessary to examine the ecl emission from this molecule as well. This butadiene did, in fact, electrochemiluminese for a short period with light characteristic of its fluorescence. This result led to a brief investigation of the fluorescence and electrochemical behavior of arylbutadienes and to the preparation of 9-methoxy-10-(4-phenyl-1,3-butadienyl)anthracene (I) as a potential electrochemiluminescent substance. The fluorescence spectra of some phenyl- and naphthyl-substituted butadienes had been the basis of a previous quantitative study.[19]

Cyclic voltammetry showed that the anion of 1-phenyl-4-(9-anthracenyl)-1,3-butadiene (E_{peak} = 1.67 v) has a lifetime of 4 sec in DMF solution, but the cation (E_{peak} = +1.04 v) has less than a 0.02-sec lifetime.

The 9-methoxy-substituted compound I showed a bathochromic shift of its fluorescence maximum in DMF solution, λ_{max}^{fluor} 560 mμ, but its fluorescence was almost entirely quenched ($\Phi = 0.007$) and, of course, no ecl emission could be detected.

Table III reports the absorption and emission characteristics of a number of 1,4-diaryl-1,3-butadienes which are not reported in the literature. Because of cation instability, the photoisomerization phenomenon,[20] and widely varying fluorescence efficiencies, these compounds have limited usefulness in the study of electrochemiluminescence.

Other Solvents. The ecl emission from 1,3,4,7-tetraphenylisobenzofuran has also been examined employing dimethyl sulfite, propylene carbonate, 1,2-dimethoxyethane, acetonitrile, trimethylacetonitrile, and benzonitrile as the solvent, replacing DMF. With all of these solvents the ecl emission, under otherwise identical conditions, is markedly dimmer and of shorter duration than in DMF. With some solvents, particularly benzonitrile, the stability of the 1,3,4,7-tetraphenylisobenzofuran cation radical is improved, as measured by cyclic voltammetry; however, this is at the expense of the stability of the anion radical. Many effects on ion solvation, current carrying, and electrode processes come into consideration when the solvent is changed in an electrochemical experiment, so it is presently impossible to rationalize these observations in a way which may aid in understanding the ecl phenomenon.

General Discussion

The ecl and cyclic voltammetry results reported here are consistent with ion radicals being intermediates in the light-emitting process. The sharp distinction seen between bright and dim ecl emitters in DMF is paralleled by the distinction between those materials having both anion and cation radicals with at least moderate stability in this solvent and those which have one or more exceedingly unstable monoion radicals. One of the most striking examples of this parallelism is seen in the behavior of the two isomeric tetraphenylisobenzofurans. The 1,3,4,7-tetrasubstituted isomer is one of the best ecl emitters while the 1,3,5,6-tetrasubstituted isomer gives barely detectable emission, this, despite the fact that the emission spectra of these two compounds are very similar and the fluorescence efficiency of the latter isomer is *even greater* than that of the former. The stabilities of the cation radicals of these isomers are very different and this property appears to have an important effect on the brightness *and* duration of ecl emission.

At this point it is reasonable to inquire into the factors which contribute to the large differences in ion-radical stabilities which are found among chemically similar species. Chemical studies have indicated that cation radicals may undergo a variety of complex reactions; however, such studies do not afford a rationalization of the differences in rates which the cyclic voltammograms reported in this investigation suggest. In the tetraphenylisobenzofurans, the 1,3 phenyls are sterically much more hindered from planarity with the isobenzofuran nucleus in the 1,3,4,7 isomer than in the 1,3,5,6 isomer. Conversely, the 5,6 phenyls would seem to be more hindered than the 4,7 phenyls. Although estimation is difficult, it would appear that the 1,3,5,6 isomer permits *greater* delocalization than the 1,3,4,7 isomer. Insofar as delocalization tends to make the cation radical less reactive, this effect seems to run contrary to the experimental results. An explanation more consistent with the experimental is that the phenyl groups function by protecting reactive positions on the isobenzofuran nucleus rather than through electronic delocalization.

Hückel molecular orbital (HMO) calculations on the isobenzofuran nucleus result in the electron deficiency

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[18] A qualitative observation of the fluorescence of this compound was previously reported; *cf.* G. Drehfahl, G. Plotner, W. Hartrodt, and R. Kühmstedt, *Chem. Ber.*, **93**, 1799 (1960).

[19] Y. Hirshberg, E. Bergmann, and F. Bergmann, *J. Am. Chem. Soc.*, 72, 5117 (1950).

[20] Y. Hirshberg, E. Bergmann, and F. Bergmann, *ibid.*, 72, 5120 (1950).

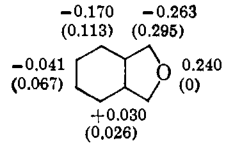

Figure 2. Electron deficiency and unpaired electron density distribution in the isobenzofuran cation radical (unpaired electron density in parentheses). Parameters employed: $\alpha_O = \alpha_C + 2.0\beta_{CC}$ and $\beta_{CO} = 0.8\beta_{CC}$.

and spin density distribution for the cation radical shown in Figure 2. On a static basis, the 4,7 positions of the isobenzofuran cation radical are calculated to be four times as electron deficient and have almost twice as much unpaired electron density as the 5,6 positions. Phenyl substituents on the more reactive 4,7 positions may thus afford the needed additional protection.

The relative values of the ion free valences at the three reactive sites as defined by Nagakura and Tanaka[21] may be a better index of their relative reactivities than the charge and unpaired electron density. The cation free valences (F_r^+) are defined[21] as $F_r^+ = F_r + f_r$, where F_r is Coulson's free valence and f_r is the unpaired or "frontier" electron density.

The free valences as well as the frontier electron densities are largest at the 1,3 positions, intermediate at the 4,7 positions, and smallest at the 5,6 positions, indicating the same order of reactivity by the ion free-valence method as found for the "frontier" electrons alone.

That the 1,3 positions of the isobenzofurans are most reactive is evident from the fact that these must be substituted in order to have an isolable compound. The utility of 4,7 disubstitution for further stabilization, especially in the cation, has not previously been appreciated.

The ion-radical stability also affects the lifetime of the electrochemiluminescence emission. It was observed that the N-methylisoindoles which had relatively stable cations emitted light for a considerably longer time (maximum, 30 hr) than the isobenzofurans (maximum, 6.75 hr). On working up these solutions after ecl emission had ceased, only the corresponding 3,6-diaryl-1,2-diaroylbenzenes could be isolated.[4] The mechanistic pathway of this reaction remains to be explored.

The concentration of fluorescer in the ecl-emitting system is an important factor in the brightness of the emission. As indicated in a preliminary communication, ~10^{-2} *M* fluorescer in DMF appears to be optimal,[1] but this concentration often cannot be achieved because of low solubility. Solubility is not a controlling influence in the distinction between bright and dim emitters, however, because 1,3-di-*p*-biphenylyl-4,7-diphenylisobenzofuran is a very bright ecl emitter at only 2 m*M* while 1,3,5,6-tetraphenylisobenzofuran is very dim even at 5m*M*.

The mechanism of the ecl emission process is not completely illuminated by recognition of the fact that moderate cation- and anion-radical stability are required for bright emission. Gross instability of one ion may mean that buildup of decomposition products deleterious to emission is very rapid. Without controlled double-potential step experiments (to be discussed in future publications), we have no experimental evidence which can differentiate between ion-radical annihilation, ion-radical reaction with decomposition product, and ion-radical electron transfer at the electrode surface (heterogeneous electron transfer). This investigation, however, provided some structure–property background which seemed necessary as a prelude to further considerations of the mechanism of the ecl process.

Experimental Section

A. Synthetic. 1,3-Diphenyl-,[9] 1,3,4,7-tetraphenyl-,[7,13] 1,3,5,6-tetraphenyl,[12] and 1,3,4,5,6,7-hexaphenylisobenzofuran[13] were prepared and purified by literature methods. 1,3,4,7-Tetraphenylisobenzothiophene,[7] 1,2,3-triphenylisoindole,[15] 2-methyl-1,3-diphenylisoindole,[16] 2,5-diphenylfuran,[22] and 2,5-di-*p*-anisylfuran[23] were also prepared according to literature methods. All isobenzofurans and isoindoles used for electrochemical and spectroscopic study were recrystallized from deoxygenated solvents (bubbled with nitrogen) under subdued light and were vacuum dried. Their infrared spectra showed no evidence of carbonyl absorption in the 1650-cm^{-1} region. Such absorption was *frequently* detected if the above precautions were not adhered to.

4,5-Di(*p*-biphenyloyl)-3,6-diphenylcyclohexene. In 400 ml of pentyl alcohol, 7.0 g (0.018 mole) of *trans*-di-(*p*-biphenyloyl)-ethylene[9] (analytically pure) and 3.72 g (0.018 mole) of *trans,trans*-1,4-diphenyl-1,3-butadiene (Eastman Kodak Co.) were refluxed for 48 hr. The solution was cooled and 100 ml of petroleum ether (bp 30–60°) was added. The precipitated product was filtered and recrystallized from ethanol, yield 9.0 g (84%) of colorless crystals, mp 176°.

Anal. Calcd for $C_{44}H_{34}O_2$: C, 88.86; H, 5.76; O, 5.38. Found: C, 87.96; H, 5.92; O, 4.99.

1,2-Di(*p*-biphenyloyl)-3,6-diphenylbenzene. A solution of 5.0 g (0.0084 mole) of 4,5-di(*p*-biphenyloyl)-3,6-diphenylcyclohexene in 200 ml of chloroform was brought to reflux, and to the refluxing solution 3.3 g of bromine in 10 ml of chloroform was added dropwise. After the addition was complete the solution was kept refluxing for an additional 20 min. The solvent was then removed, and the residue was taken up in methanol, filtered, and recrystallized from butyl acetate. A yellow solid, mp 266–268°, was obtained which was not the desired product. By adding petroleum ether to the mother liquor a colorless product was obtained, which after recrystallization from butyl acetate had mp 225°, yield 1.87 g (36%).

1,3-Di-*p*-biphenylyl-4,7-diphenylisobenzofuran. To a solution of 3 g of sodium hydroxide in 200 ml of ethanol was added 1.5 g of 1,2-di(*p*-biphenyloyl)-3,6-diphenylbenzene. To the refluxing solution 3.0 g of activated zinc was added, and refluxing was continued for 1 hr. The hot solution was filtered into 200 ml of glacial acetic acid. By adding 50 ml of water, a yellow-green solid separated which was filtered and dried in a desiccator. The product was recrystallized from benzene (in a dark room, under argon) yielding 150 mg of yellow crystals with mp 240–241°. Hexane was added to the mother liquor and a further 330 mg of the product with mp 239–240° was obtained, yield 480 mg (33.1%).

Anal. Calcd for $C_{44}H_{30}O$: C, 91.95; H, 5.25; O, 2.78. Found: C, 91.41; H, 5.42; O, 2.09.

3-Phenyl-4,5-dibenzoyl-6-(9-anthracenyl)cyclohexene. A mixture of 4.50 g (0.015 mole) of 1-phenyl-4-phenyl-4-(-anthracenyl)-1,3-butadiene[18] and 3.47 g (0.15 mole) of 1,2-dibenzoylethylene (Eastman Kodak Co.) was heated for 3 hr at 150–160°. The product was recrystallized from benzene–petroleum ether to give 2.81 g of crystals with a crude melting point of 105–115°.

1-Phenyl-2,3-dibenzoyl-4-(9-anthracenyl)benzene. The crude 3-phenyl-4,5-dibenzoyl-6-(9-anthracenyl)cyclohexene (2.81 g, 0.0047 mole) was dissolved in 10 ml of refluxing chloroform, and 1.74 g (0.0097 mole) of bromine in 10 ml of chloroform was added. After refluxing the solution for 15 min, the chloroform was removed *in vacuo* and the residue was recrystallized from ethanol to give 0.77 g of crystals, mp 217–219°.

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1,3,4-Triphenyl-7-(9-anthracenyl)isobenzofuran. A mixture of 0.7 g (0.0012 mole) of the above 1-phenyl-2,3-dibenzoyl-4-(9-anthracenyl)benzene and 2.0 g of potassium hydroxide in 100 ml of ethanol was refluxed for 30 min. To the hot solution 2.0 g of activated zinc was added and refluxing was continued for 1 hr. The hot solution was filtered directly into 100 ml of glacial acetic acid and the acetic acid solution was refluxed for 20 min, cooled, and diluted with a large excess of water. The yellow precipitate was removed by filtration, dissolved in benzene, and chromatographed with benzene on alumina. The yellow fluorescent fraction was isolated (a blue fluorescent fraction was also present, but was not investigated), 70 mg, which had mp 218–220°.

Anal. Calcd for $C_{40}H_{26}O$: C, 91.92; H, 5.01. Found: C, 91.74; H, 5.27.

4,5-Di-*p*-anisoyl-3,6-diphenylcyclohexene. A solution of 5.92 g (0.02 mole) of 1,2-di(*p*-anisoyl)ethylene[24] and 4.12 g of 1,4-diphenyl-1,3-butadiene in 500 ml of pentyl alcohol was refluxed for 30 hr. After cooling, 100 ml of petroleum ether was added to the solution and the precipitated product was filtered and recrystallized from ethanol to yield 8.0 g (77%), mp 165°.

Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.25; H, 6.02; O, 12.73. Found: C, 80.71; H, 6.00; O, 12.36.

1,2-Di-*p*-anisoyl-3,6-diphenylbenzene. A solution of 8 g (0.016 mole) of 4,5-di-*p*-anisoyl-3,6-diphenylcyclohexene in 300 ml of chloroform was brought to reflux. To the refluxing solution 5.12 g (0.032 mole) of bromine in 50 ml of chloroform was added dropwise, avoiding an excess of bromine in the reaction mixture. After the addition was complete, refluxing was continued for 20 min. The solvent was evaporated and the yellow solid residue was taken up in a small amount of methanol, filtered, and recrystallized from ethanol to yield 5.0 g (63%) of a colorless solid, mp 204–206°.

1,3-Di-*p*-anisyl-4,7-diphenylisobenzofuran. A solution of 9.0 g of sodium hydroxide in 500 ml of ethanol containing 4.5 g (0.009 mole) of 1,2-di-*p*-anisoyl-3,6-diphenylbenzene was refluxed for 15 min. To the hot solution 9.0 g of activated zinc was added and refluxing was continued for 1 hr. The hot mixture was filtered into 500 ml of glacial acetic acid, and by adding a small amount of water a yellow precipitate was obtained, which was twice recrystallized from cyclohexane (under N_2), yielding 0.85 g (19.5%) of yellow crystals, mp 226°.

Anal. Calcd for $C_{34}H_{26}O_3$: C, 84.62; H, 5.43; O, 9.95. Found: C, 83.94; H, 5.50; O, 9.43.

4,5-Dibenzoyl-3,6-di-*p*-anisylcyclohexene. 1,2-Dibenzoylethylene, 4.62 g (0.2 mole), and 5.32 g (0.02 mole) of di-*p*-anisyl-1,3-butadiene[20] were mixed and heated at 150–160° for 3.5 hr. The fused mass was taken up in ethanol, filtered, and recrystallized from ethanol to give colorless crystals, mp 144–147°, yield 7.6 g (76.5%). The nmr spectrum agreed with the assigned structure.[25]

1,2-Dibenzoyl-3,6-*p*-anisylbenzene. A solution of 5.02 g (0.01 mole) of 4,5-dibenzoyl-3,6-di-*p*-anisylcyclohexene in 300 ml of chloroform was heated to reflux. To the refluxing solution 3.20 g (0.02 mole) of bromine in 50 ml of chloroform was added dropwise, avoiding an excess of bromine. After the addition was complete the solution was refluxed for 10 min and the solvent was evaporated. The brown residue was taken up in methanol, filtered, and recrystallized from benzene–cyclohexane (charcoal) yielding 3.33 g (66.5%) of colorless crystals, mp 207–208°.

Anal. Calcd for $C_{34}H_{26}O_2$: C, 81.91; H, 5.26; O, 12.84. Found: C, 81.51; H, 5.25; O, 12.99.

1,3-Diphenyl-4,7-di-*p*-anisylisobenzofuran. 1,2-Dibenzoyl-3,6-di-*p*-anisoylbenzene, 3.0 g (0.006 mole), was added to a solution of 6.0 g of potassium hydroxide in 300 ml of ethanol and refluxed for 30 min; 6.0 g of activated zinc was added to the hot solution and refluxing was continued for 1 hr. The hot mixture was filtered into 300 ml of glacial acetic acid, water was added, and the yellow precipitate was filtered, dried in a desiccator, and twice recrystallized from benzene–heptane yielding 0.48 g (16.5%) of yellow crystals, mp 195–196°.

Anal. Calcd for $C_{34}H_{26}O_3$: C, 84.62; H, 5.43. Found: C, 85.05; H, 5.23.

4,5-Di-*p*-anisoyl-3,6-di-*p*-anisylcyclohexene. Di(*p*-anisoyl)ethylene, 5.92 g (0.02 mole), was mixed with 5.32 g (0.02 mole) of 1,4-di-*p*-anisyl-1,3-butadiene and heated at 160–170° for 3.5 hr. The brown mass was taken up in ethanol, filtered, and recrystallized from ethanol, yield 10.8 g (96%), mp 143–145°. The nmr spectrum was in agreement with the structure.[25]

1,2-Di-*p*-anisoyl-3,6-di-*p*-anisylbenzene. A solution of 5.62 g (0.01 mole) of 4,5-di-*p*-anisoyl-3,6-di-*p*-anisylcyclohexene in 300 ml of chloroform was heated to reflux, and 3.20 g (0.20 mole) of bromine in 50 ml of chloroform was slowly added to the refluxing solution. After the addition was complete, refluxing was continued for 10 min and the solvent was evaporated. The residue was taken up in methanol, filtered, and recrystallized from benzene–cyclohexane (charcoal) yielding colorless crystals, mp 188–189°, 3.4 g (61%).

1,3,4,7-Tetra-*p*-anisylisobenzofuran. A solution of 3.0 g (0.0055 mole) of 1,2-di-*p*-anisoyl-3,6-di-*p*-anisylbenzene and 6.0 g of potassium hydroxide in 300 ml of ethanol was refluxed for 0.5 hr. To the hot solution was added 6 g of activated zinc, and refluxing was continued for 1 hr. The hot solution was filtered into 300 ml of glacial acetic acid. Yellow crystals separated from the cooling solution and were filtered, dried in a desiccator, and recrystallized twice from a benzene–cyclohexane mixture (1:3) giving 250 mg (8.6%) of green-yellow crystals, mp 233–235°.

Anal. Calcd for $C_{36}H_{30}O_5$: C, 79.68; H, 5.57. Found: C, 79.65; H, 5.56.

N-Methyl-2,3,6,7-tetraphenylisoindole. A mixture of 3.5 g (0.008 mole) of 1,2-dibenzoyl-3,6-diphenylbenzene and a fourfold excess of methylammonium formate[26] was heated at 190–195° for 15 hr. After this time yellow-green crystals had separated in the hot solution. After cooling to ambient temperature, methanol was added to the solution and the product was filtered off and twice recrystallized from benzene to yield 1.5 g (35%), mp 281–283°.

Anal. Calcd for $C_{33}H_{25}N$: C, 91.00; H, 5.79; N, 3.22. Found: C, 90.88; H, 5.76; N, 3.31.

N-Methyl-2,7-di-*p*-anisyl-3,6-diphenylisoindole. A mixture of 4 g (0.008 mole) of 1,2-di-*p*-anisoyl-3,6-diphenylbenzene and 15 ml of methylammonium formate[26] was refluxed (210–215°) for 24 hr under nitrogen. The solution was cooled and the crystals were filtered off and recrystallized twice from benzene–petroleum ether to yield 1.46 g (40%), mp 237–239°.

Anal. Calcd for $C_{35}H_{29}NO_2$: C, 84.82; H, 5.90; N, 2.83. Found: C, 84.52; H, 5.89; N, 2.86.

1,4-Diarylbutadienes. 1,4-Di-*p*-biphenylyl-1,3-butadiene,[18] 1-phenyl-4-(1-naphthyl)-1,3-butadiene,[20] 1,4-di(1-naphthyl)-1,3-butadiene,[27] and 1-phenyl-4-(9-anthracenyl)-1,3-butadiene[18] were prepared by methods described in the literature.

1-Phenyl-4-*p*-cyanophenyl-1,3-butadiene. To a mixture of 3.64 g (0.028 mole) of *p*-cyanobenzaldehyde (Aldrich Chemical Co.) and 10.0 g (0.022 mole) of cinnamyltriphenylphosphonium bromide (Aldrich Chemical Co.) in 90 ml of ethanol was added 140 ml of a 0.2 *M* solution of lithium ethylate in ethanol. The mixture was refluxed for 2 hr and the solution was concentrated by distillation of most of the ethanol. On cooling, the precipitated product was filtered and recrystallized from methanol to give 1.04 g (20%) of colorless crystals, mp 163–164°.

Anal. Calcd for $C_{12}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.98; H, 5.74; N, 6.41.

9-Methoxy-10-(4-phenyl-1,3-butadienyl)anthracene. To a mixture of 2.3 g (0.005 mole) of cinnamyltriphenylphosphonium bromide and 1.18 g (0.005 mole) of 10-methoxy-9-anthraldehyde[28] in 50 ml of ethanol was added 0.20 g (0.29 g-atom) of lithium metal treated with 50 ml of ethanol. The reaction mixture was refluxed 2 hr, then cooled, diluted with water (100 ml), and allowed to stand overnight. The precipitate was filtered and recrystallized from ethanol. The dark product was sublimed at 140° (0.01 mm), and the orange-yellow sublimate was recrystallized from methanol to give golden yellow crystals, mp 133–135°.

Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.74; H, 5.86.

B. Reagents. Reagent grade DMF was purified by heating for several hours at 90° over sodium hydroxide, passed through a column of 4A molecular sieves, and then fractionated under vacuum. All solutions were prepared in a dry atmosphere and the prepurified nitrogen used for final deaeration was passed over hot copper turnings to remove traces of oxygen. Spectroscopic grade acetonitrile was stored over sodium carbonate and distilled from potassium

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[25] The nmr spectra and conformational analysis of the cyclohexenes reported here are the subject of a paper in preparation.

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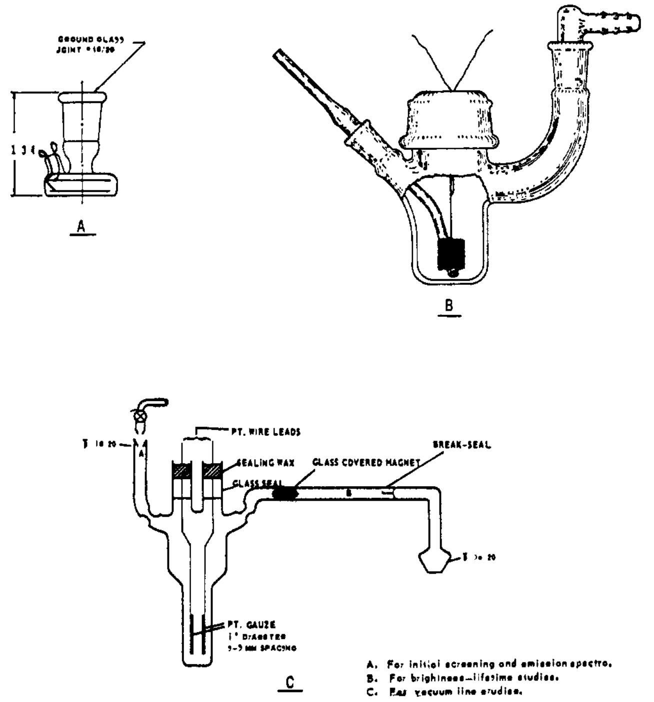

Figure 3. Electrochemiluminescence cells.

permanganate before use. Propylene carbonate (Jefferson Chemical Co.), dimethyl sulfite (Eastman Kodak Co.), trimethylacetonitrile (Aldrich Chemical Co.), and benzonitrile (Eastman Kodak Co.) were dried by passing through a column of 4A molecular sieves and then fractionated under nitrogen or vacuum. 1,2-Dimethoxyethane (Ansul Chemical Co.) was distilled from lithium aluminum hydride under nitrogen.

Polarographic grade tetrabutylammonium perchlorate, purchased from Southwestern Chemical Co., was dried in air and stored in a vacuum desiccator over phosphorus pentoxide.

C. Electrochemiluminescence Emission. The cell employed for initial screening of ecl emitting substances is shown in Figure 3A. The volume of this cell is 4.2 ml, and it was filled under nitrogen. The cell design permits mounting in front of a combination spectroradiometer–fluorimeter[29] which was used for obtaining the ecl emission spectrum and for qualitative fluorescence spectra. Quantitative fluorescence emission spectra, including spectral response corrections, and quantum yield measurements were performed as previously described.[29] No significant spectral differences could be detected between the ecl emission and the fluorescence emission of the compounds studied herein.

Relative brightness and lifetime measurements of ecl emitting species were made in the cell shown in Figure 3B. The brightness measurements were obtained with a Photo Research Corp. Model UB 1/2 spectral brightness meter which was focused near the center of the front electrode of the cell. A 5 m*M* solution of 1,3,4,7-tetraphenylisobenzofuran (15 ml) in a DMF solution which was 0.1 *M* in tetra-*n*-butylammonium perchlorate and which was purged with a stream of argon or oxygen-free nitrogen gave an initial brightness reading of 10.8 foot-lamberts in this cell when 8.0 v (60 cps) was imposed across the electrodes. In 95 min the intensity of this emission was reduced to 0.01 foot-lambert. When 7.0 v was applied across the cell, using a new solution and clean electrodes, the initial brightness was 8.0 foot-lamberts, and it required 225 min for the emission to be reduced to 0.01 foot-lambert. Applying 6.0 v resulted in an initial brightness of 1.7 foot-lamberts and a lifetime of 405 min to 0.01 foot-lambert.

The square-wave input to all three cells was provided by a transistorized switch which alternated between the positive and negative outputs of two Trygon Electronics HR 20-5A DC power supplies.

The cell employed for emission studies on a vacuum line system is illustrated in Figure 3C. Differences in cell geometries prevented direct comparison of the results obtained with this cell and with the others. Although here the fluorescers and electrolyte were pumped on for 48 hr at 10 μ, and the solvent was transferred to the cell by bulb-to-bulb distillation from storage over molecular sieves, before the cell was sealed off, no significant differences in lifetime or brightness could be detected from the more simply handled systems.

A three-electrode operational amplifier-based electronic polarograph was used to record the cyclic voltammograms in conventional cells. The ultraviolet absorption spectra were measured on a Cary 14 spectrophotometer. Dropping mercury electrode polarograms were obtained on a Leeds and Northrup electrochemograph, Type E.[30]

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