the laser pulse (~250 ns) in oxygenated solution (Figure 1a,b, at 410 nm). Addition of 1 mM diphenyldiazomethane led to a well-resolved signal buildup which occurs with a lifetime of 3 μs (Figure 1c) and leads to the spectrum of Figure 2 (top). The 410-nm band in this spectrum is identical with that of the carbonyl oxide recently characterized in the reaction of diphenylcarbene with oxygen (Figure 2, bottom).[8] The same spectrum can also be obtained in the reaction mixture described above, when the laser excitation wavelength is 337.1 nm[18] instead of 587 nm. However, in this case the formation of the carbonyl oxide is much faster (see Figure 1d) reflecting the rapid reaction of oxygen with diphenylcarbene ($k_{O_2} = 5 \times 10^9$ M^{-1} s^{-1}).[8] The small buildup that follows the jump in trace d, Figure 1, reflects minor light adsorption by MB at 337.1 nm. We suggest that the same intermediate is produced by two different reaction mechanisms depending on the excitation wavelength, according to Scheme I

Scheme I

587 nm, singlet route

$$MB \xrightarrow{h\nu} \rightarrow MB^*$$

$$\mathrm{MB^* + O_2 \rightarrow MB + {}^1O_2}$$

$$\mathrm{{}^1O_2 + Ph_2CN_2 \rightarrow N_2 + Ph_2COO}$$

337 nm, triplet route

$$\mathrm{Ph_2CN_2 \xrightarrow{h\nu} {}^1(Ph_2C:) \rightarrow {}^3(Ph_2C:)}$$

$$\mathrm{{}^3(Ph_2C:) + O_2 \rightarrow Ph_2COO}$$

(where all secondary reactions and nonreactive decay modes have been excluded). We note that the MB mechanism (Figure 2, top) also leads to weak, irreversible bleaching at 650 nm, presumably due to side reactions leading to some MB consumption.

The kinetics of the reaction $^1O_2$ with diphenyldiazomethane were monitored by examining the pseudo-first-order growth at 410 nm as a function of diazo concentration and led to $k \sim 6 \times 10^8$ M^{-1} s^{-1} in agreement with the value reported by Bethell et al.[19] The long-lived carbonyl oxide (>100 μs) can be trapped by aldehydes and electron-deficient and electron-rich olefins;[20] in the case of 2,5-dimethyl-2,4-hexadiene (DMHD), the rate constant observed was $\sim 1 \times 10^6$ M^{-1} s^{-1}, in agreement with the value obtained earlier from the carbene route.[8] Traces e and f in Figure 1 illustrate the effect of the diene; in both cases the carbonyl oxide lifetime is significantly shortened. In the carbene mechanism (trace e) the decrease in signal intensity is minor; however, in trace f we observe a drastic decrease, which we attribute to singlet oxygen scavenging by the diene,[21] and possible triplet MB quenching. We have also examined the trapping of the carbonyl oxide by aldehydes; these reactions are well characterized[10,22] and yield the corresponding ozonides. The rate constants in acetonitrile are $(2.1 \pm 0.2) \times 10^6$ and $(3.1 \pm 0.4) \times 10^6$ M^{-1} s^{-1} for phenylacetaldehyde and acetaldehyde, respectively.

We also examined the effect of 2,3-dimethyl-2-butene (TME) on the yield of carbonyl oxide produced by the singlet route. Stern-Volmer analysis of these data yields the rate constant for reaction of $^1O_2$ with TME as 3.5×10^7 M^{-1} s^{-1} in acetonitrile in excellent agreement with reported values.[23]

It has been proposed[10] that $^1O_2$ reacts with diazo compounds via the intermediacy of the five-membered ring azo peroxide. If such an intermediate is involved,[24] it must be short lived in the time scale of our experiments, since the 410-nm band is identical with that produced via the carbene and its generation rate is linearly dependent on diazo concentration.

Note Added in Proof. The reaction of fluorenone oxide with DMHD has now been studied. The results suggest that oxidation products generated in situ can lead to somewhat overestimated rates for DMHD. This may also apply to benzophenone oxide.

Registry No. $\mathrm{Ph_2CN_2}$, 883-40-9; $\mathrm{O_2}$, 7782-44-7; $\mathrm{Ph_2C:}$, 3129-17-7; $\mathrm{Ph_2CO\text{-}O}$, 86508-70-5.

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[17] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747-7753.

[18] Using a Molectron UV-24 nitrogen laser giving 8-10-ns pulses of up to 10 mJ at 337.1 nm.

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[21] Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244-7253.

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[23] Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809-999.

[24] This proposal[10] is based on the detection of $\mathrm{N_2O}$ among the reaction products. An alternate route to this product may be the reaction of $\mathrm{Ph_2COO}$ with $\mathrm{Ph_2CN_2}$ which occurs with $k \sim 4 \times 10^5$ M^{-1} s^{-1}.[8]

Principal Component Analysis Applied to 1-Phenyl-2-(2-naphthyl)ethene Fluorescence. Four Components not Two

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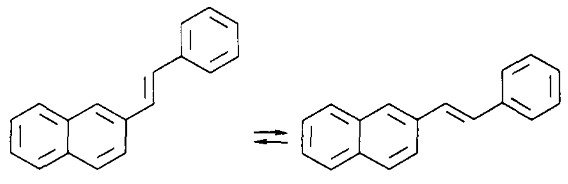
The complex photophysical behavior of 1-phenyl-2-(2-naphthyl)ethene (2-NPE) has been attributed to the presence of an equilibrium mixture of aryl-rotational conformers:



2-NPE$_1$ 2-NPE$_2$

Electronic excitation increases the double-bond character in the aryl-vinyl bonds "freezing" ground-state conformers into noninterconverting populations of excited-state species.[1] The dependence of fluorescence spectral shape on excitation wavelength, λ_{exc}, and fluorescence decay results requiring multiexponential fits[1,2] are accounted for since the spectra and excited-state lifetimes of such conformers should differ. Such properties are exhibited by 1,2-diarylethenes capable of existing in multiple, nearly isoenergetic, ground-state conformers[3] and are absent in olefins substituted with symmetrical aryl groups or in olefins in which a single conformer predominates for steric reasons.[1,4] We have employed two approaches in an effort to determine conclusively the role of 1-α aryl rotation in the 2-NPE system, to obtain pure component spectra, and to assign their structure and lifetime(s).[6] The first was treatment of *t*-2-NPE fluorescence spectra obtained under varying conditions of λ_{exc}, T, η, and quencher, Q, in terms

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[1] For reviews, see: (a) Fischer, E. *J. Photochem.* **1981**, *17*, 231. (b) Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705.

[2] For key references, see: (a) Haas, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* **1978**, *82*, 1638. (b) Birks, J. B.; Bartocci, G.; Aloisi, G. G.; Dellonte, S.; Barigelleti, F. *Chem. Phys.* **1980**, *51*, 113.

[3] For recent examples, see: Wismontski-Knittel, T.; Das, P. K.; Fischer, E. *J. Phys. Chem.* **1984**, *88*, 1163.

[4] We are concerned here with fluorescence arising from equilibrium distributions of vibronically excited molecules associated with each extreme conformer structure. As pointed out by a referee, at low temperature medium rigidity may give rise to further λ_{exc} dependence of fluorescence from olefins having either symmetrical or unsymmetrical aryl substituents, because the medium may prevent equilibration of torsionally excited molecules prior to emission. Pertinent examples are provided by biphenyl and 2-phenylnaphthalene.[5]

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[6] Eaker, D. W. Ph.D. Dissertation, Florida State University, Tallahassee, 1984.

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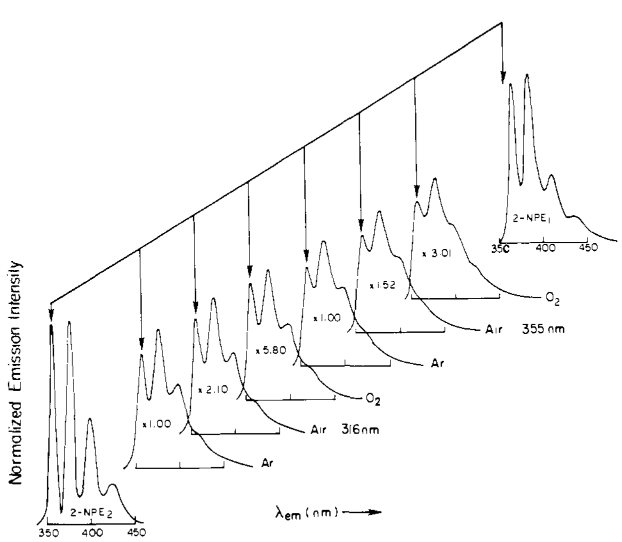


Figure 1. Typical 2-NPE fluorescence spectra in the presence of argon, air, and O_2 at two λ_{exc}. Numbers are relative normalization factors. PCOMP component spectra are given at either end. The arrows indicate position of $\lambda = 357$ nm for each spectrum.

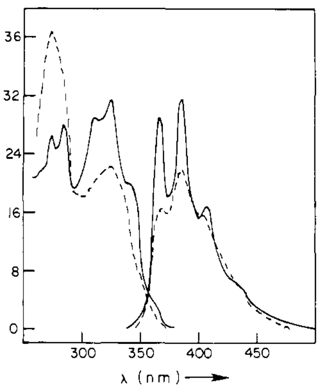
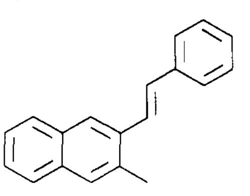
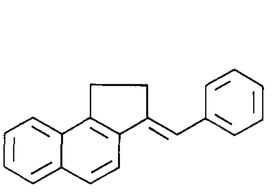


Figure 2. Absorption and fluorescence spectra of *t*-MPE (---) and *t*-BPE (—) in methylcyclohexane. Fluorescence intensity is arbitrary: $\phi_f = 0.52$ and 4.8×10^{-3} for *t*-MPE and *t*-BPE at 25 °C, respectively.

of intrinsic properties of component species by application of principal component analysis (PCOMP), a curve resolution technique.[7] The second was synthesis and study of conformationally restricted analogues: 1-phenyl-2-(3-methyl-2-naphthyl)ethene (MPE) and 3-styrylidenebenz[*e*]indane (BPE).



MPE



BPE

We report here the PCOMP resolution of *t*-2-NPE fluorescence spectra under varying λ_{exc} and oxygen concentration and their relationship to the analogue spectra.

Fluorescence spectra of the trans isomers of 2-NPE, MPE, and BPE (10^{-5} M in methylcyclohexane, 26 °C, measured by using a Hitachi MPF-2A spectrofluorimeter,[8] were corrected for nonlinear instrumental response.[8b] Fluorescence quantum yields, ϕ_f, were determined relative to quinine sulfate standard, $\phi_f = 0.55$.[9]

Table I. PCOMP Analysis of 2-NPE Fluorescence Quenching by Molecular Oxygen[a]

$[O_2]10^3$,[b] M	λ_{exc}, nm	ϕ_f^{obsd}	x_1	ϕ_1^0/ϕ_1	ϕ_2^0/ϕ_2
0	316	0.50	0.421	1.00	1.00
2.07		0.24	0.434	2.01	2.11
9.88		0.086	0.446	5.47	6.11
0	355	0.58	0.509	1.00	1.00
2.07		0.38	0.527	1.47	1.58
9.88		0.19	0.536	2.87	3.19

[a] Methylcyclohexane, 26 °C. [b] See: Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623.

Changes in 2-NPE fluorescence spectral shape with λ_{exc} and in fluorescence intensity with $[O_2]$ were in excellent agreement with those reported previously (Figure 1).[1,2,10] The fluorescence spectra of MPE and BPE were insensitive to changes in λ_{exc} (Figure 2).

Applications of the PCOMP method to the analysis of emission spectra have been described.[11,12] PCOMP spectroexcitational emission input matrices (30 × 30) were employed, each row of which represented a digitized and normalized 2-NPE fluorescence spectrum (examples shown in Figure 1) obtained at one of several λ_{exc} in the presence or absence of O_2. Matrix columns differed by 2.5- or 5-nm increments over a λ range spanning the fluorescence spectra. Recognition of the major components was based on the magnitude of the eigen values, which were in general $\geq 10^{12}$ times larger than those considered negligible.[7,11,12] Inclusion of all nonnegligible components was assured since accepted solutions accounted for >99% of the total variance of the measured spectra. Resolved component spectra are shown at the extremes of Figure 1.[13] They agree well with those obtained by Fischer at −185 °C at different λ_{exc}.[2a] The 0–0 bands of the resolved spectra are displaced by ~8 nm from each other (357 and 365 nm, respectively), and, since a vibronic progression of ~1430 cm⁻¹ is apparent in each, good correspondence exists between maxima and minima of the two spectra.

The analogue fluorescence spectra (Figure 2) have maxima at wavelengths matching closely those of the 365-nm 2-NPE component spectrum. Comparison of *trans*-stilbene, *trans-o*-methylstilbene,[14] and *trans*-biindanylidene[8a] spectra shows that methyl substitution should have no effect, whereas the five-membered ring should red shift the spectra. The BPE absorption spectrum, while similar in shape to that of 2-NPE,[2] is indeed red shifted by ~8 nm. It follows that the short-wavelength component is BPE-like while the long-wavelength component is MPE-like, and the spectra in Figure 1 are so labeled. This assignment confirms one based on the quasiline fluorescence spectrum of 2-NPE_2 obtained at 4 K in *n*-hexane polycrystalline matrices.[15] The PCOMP treatment gives also fractional contributions, x_i, of each component spectrum to the normalized experimental spectra. For a two-component system, observed fluorescence quantum yields are given by $\phi_f^{obsd} = (x_1 + x_2)/N$ where the normalization factor N of each spectrum is defined by $N\phi_f^{obsd} = 1$. Effective component quantum yields, x_i/N, for 2-NPE can be expressed as

$$x_1/N = (1 + \epsilon_2/(\epsilon_1 K))^{-1}\phi_1 \qquad x_2/N = (1 + \epsilon_1 K/\epsilon_2)^{-1}\phi_2$$

where ϵ_1 and ϵ_2 are the molar absorptivities of the two components at λ_{exc}, $K = [C_1]/[C_2]$ is the conformational equilibrium constant

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(13) All major spectral features of this solution were reproduced by a series of solutions obtained from spectra measured under a variety of experimental conditions.[6] Two-component solutions were found in all cases except those in which quenching led to emissive exciplexes (e.g., tri-*n*-butylamine). In the latter an additional third exciplex component was identified by PCOMP.[6]

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in the ground state, and the ϕ_i are inherent component quantum yields.

Table I gives data for the spectra in Figure 1. Analysis of such data in terms of ϕ_i will be published later. It suffices here to consider the dependence of x_i and x_i/N ratios on $[O_2]$ at the two λ_{exc} (last two columns of Table I). The striking result is that x_1 is remarkably insensitive to $[O_2]$ as should have been expected from the insensitivity of spectral shape to $[O_2]$. Furthermore, Stern–Volmer plots of component quantum yield ratios (Table I) show that the effective component lifetime depends on λ_{exc}: for λ_{exc} = 316 nm, $k_q\tau$ = 450 and 516 M^{-1}, and for λ_{exc} = 355 nm, $k_q\tau$ = 186 and 217 M^{-1} for 2-NPE$_1$ and 2-NPE$_2$, respectively. Clearly, the notion that one of the spectral components is short-lived (2–5 ns)[1,2,16] while the other is long-lived (19–27 ns)[1,2] is incorrect. *Each spectral component is long- and short-lived, the lifetime mix depending on λ_{exc}.* Assuming $k_q = 3.0 \times 10^{10}$ $M^{-1}\ s^{-1}$ for O_2 quenching,[17] effective lifetimes are τ_1 = 15 and 6.2 ns and τ_2 = 17 and 7.2 ns for 316- and 355-nm excitation, respectively. The conclusion that each spectral component has prompt and delayed contributions invalidates Birks' elegant attempt to resolve fluorescence and absorption spectra on the basis of an analysis of diexponential decay parameters.[1b,2b] An explanation of the results can be based on the theoretical prediction that for 2-NPE$_2$ the first absorption band includes a "forbidden" transition which lies somewhat below the "normal" first transition.[18] Direct excitation into the "normal" states may give rise to the short-lived emissions, while excitation into the "forbidden" states may give rise to the delayed emissions. The involvement of forbidden states also become apparent when one compares effective and theoretical radiative rate constants.[6]

Acknowledgment. We thank Professor T. J. Aartsma for suggesting to us the use of PCOMP. This work was supported by NSF Grants CHE 80-26701 and CHE 84-00706. D.W.E. thanks the National Science Foundation for a predoctoral graduate research followship, 1979–1982.

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Electrochemically Induced Pericyclic Reactions. A Radical Anionic Cyclization

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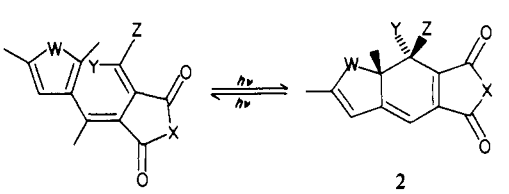
Recently we have discovered a high-yield triene-like electrocyclization which is initiated by a reversible single-electron reduction. Its occurrence provides a direct experimental test of stereochemical preference in doublet pericyclic reactions[1] and represents, to our knowledge, the first example of a six-atom electrocyclization mediated by *reversible* electron exchange.

The photochemistry and electrochemistry of compounds **1** were studied. All compounds showed strong absorption bands in the long-wavelength ultraviolet region as well as quasi-reversible cyclic voltammetric waves at about −2 V. Previous study[2-4] had established that **1a–c** react by conrotatory[3] six-electron cyclization upon photoexcitation, producing the highly colored cyclic compounds **2a–c**, respectively, eq 1. The intense red-to-orange coloration of **2** arises from its extended conjugation compared to the open form of the highly nonplanar π system of **1**.

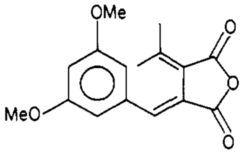


1 **2** (1)

a, W = X = O; Y = Z = CH_3
b, W = X = O; Y = H; Z = CH_3
c, W = X = O; Y, Z = adamantylidene
d, W = S; X = O; Y = Z = CH_3
e, W = S; X = NPh; Y = Z = CH_3
f, W = S; X = p-$NO_2C_6H_4N$; Y = Z = CH_3
g, W = S; X = NCH_2CO_2H; Y = Z = CH_3
h, W = S; X = NBz; Y = Z = CH_3

Analogous photocyclization was also observed for **1d–g**, affording **2d–g** in high chemical yield. With **1h**, however, the initial photocyclization product **2h** proved to be photolabile.

The phenyl **3** and naphthyl **4** analogues of these heterocycles failed to cyclize upon excitation, presumably because of the energetic cost for disruption of ring aromaticity in the transition state.



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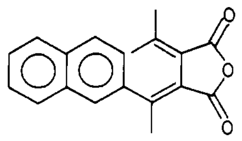

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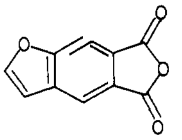

5

Controlled potential one-electron electrochemical reduction[5] of compounds **1a**, **1b**, **1d**, and **1h** in partially deaerated acetonitrile led to efficient formation of cyclized products.[6] Compounds **1c**, **1e–g**, **5**, and **6** resisted electrochemical cyclization, although stable radical anion solutions were formed in deoxygenated solution.[7] Detailed analytical electrochemical investigation of **1** gave no evidence for two-electron reduction or for the disproportionation of the initially generated monoanions to dianions. Preparative one-electron oxidation of **1** did not result in cyclization.

We propose that the observed electrocyclization occurs through the intermediacy of the radical anion as in eq 2. Radical ion electrocyclization may be facilitated by a flattening of the π system in the radical anion which allows for effective overlap of the termini of the six carbon atom system. MNDO calculations[8] indicate, for example, that the dihedral angle between the furan ring of

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(1) (a) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1977**, *99*, 23. (b) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577.

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(4) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

(5) Electroreductions were conducted in a divided electrochemical cell at a Pt working electrode in dry tetrahydrofuran containing 0.1 M tetrabutylammonium perchlorate. Both cyclic voltammetric measurements and preparative electrolyses were conducted on a Princeton Applied Research Electrochemical System. Preparative electrolyses were conducted at a constant potential of −2.1 V.

(6) The assignment of structures to **2a**, **2b**, and **2d** was based on the identity of the isolated electrolysis products with those obtained by photolysis of **1a**, **1b**, and **1d**. The structure assigned to **2h** was based on its spectroscopic properties and by the demonstration that it could be converted by photolysis to the product obtained by excitation of **1h**. Quasi-reversibility of the cyclic voltammetric reduction wave of **1a**, **1b**, and **1d** is consistent with at least partial cyclization to **2**.

(7) Intensely colored solutions were obtained upon preparative reduction of **1d–g**. The color faded immediately upon exposure to oxygen, with starting material being isolated as the only monomeric species. If oxygen is excluded, low cyclization yields are found.

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