Irradiation of 2,3-benzo-11-diazofluorene generates the carbene 2,3-benzo-11-fluorenylidene. This carbene was detected in frozen media by EPR and optical spectroscopy and shown to have a triplet ground state. The carbene was detected in fluid solution at room temperature by nanosecond and picosecond laser spectroscopy. The reactions of the carbene with methyl alcohol, cyclohexane, and α-methylstyrene were examined. Direct photolysis, triplet sensitization, and analysis of the reaction kinetics all show that the singlet state of the carbene is present in equilibrium with the triplet in significant concentration. The energy gap between the ground-state triplet and the first singlet state (ΔG₆₇) is estimated to be less than or equal to 1.0 kcal/mol. The properties of this carbene are compared with those of fluorenylidene, and a correlation of carbene structure and reactivity is suggested.

The investigation of the chemical and physical properties of aromatic carbenes (Ar₂C=) has focused recently on the influence of structure on the energy difference (ΔG₆₇) between the lowest electronic states of these intermediates. The ground state of methylene (the prototypical aromatic carbene) has been shown to be a bent triplet (3B) that is believed to be ca. 10 kcal/mol above the triplet. Recently we reported that for fluorenylidene (FL) this energy difference is decreased to less than 1.9 kcal/mol and that for 9-mesityl-9,10-dihydro-9-boraanthrylidene (BA) the difference increases to more than 5.2 kcal/mol.

The seemingly small changes in the energy separating the triplet state of a carbene from its singlet state in fact has a remarkable influence on the chemical properties of these intermediates. This conclusion can be traced to a competition between the bimolecular reactions of the ground-state carbene and the equilibration with and reaction from its upper state. Thus it is of some interest to identify those structural features that play important roles in controlling the relative energies of the singlet and triplet states of these carbenes.

To this end we have continued the investigation of the chemical and physical properties of aromatic carbenes. In this report we describe the analysis of 2,3-benzo-fluorenylidene (BFL) by a combination of picosecond and nanosecond laser spectroscopy with conventional chemical probes. In related papers we present the results of similar investigations of 3,6-dimethoxyfluorenylidene and of 9-xanthylidene. The findings from these studies combined with those previously reported permit the clear identification of several major factors controlling the properties of aromatic carbenes.

![Figure 1. Curie law plot for 3BFL.](image)

at low temperature gives a paramagnetic species readily identified as triplet fluorenylidene (3BFL). The

\[ \text{BDAF} \xrightarrow{\text{hv}} \text{BFI} \]

(1) Photolysis of BDAF in Frozen Media. Irradiation of BDAF in a 2-methyltetrahydrofuran (MTHF) glass

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1Department of Physics.
Chemical and Physical Properties of 2,3-Benzofluorenylidene

Figure 2. (A) Absorption spectrum recorded at 77 K from irradiation of BDAF (solid line), before irradiation (dotted line), and after warming the irradiated sample to room temperature and recooling to 77 K (dashed line). (B) Absorption spectrum recorded 50 ps after irradiation of BDAF in cyclohexane. Note the difference in wavelength scales between A and B. There is no probe light below ca. 440 nm and no detectable absorption above 550 nm in the picosecond experiment.

Zero-field parameters obtained from fitting the usual spin Hamiltonian are |D| = 0.39 cm⁻¹ and |E| = 0.030 cm⁻¹. These values are quite similar to those observed for fluorenylidene and are thus indicative of the nearly identical geometry at the carbene carbon for these two triplet species.

The ground state of BFL is identified as the triplet by comparison of the results from the electron resonance analysis of the Curie law plot (Figure 1). The EPR signal observed at 770 G increases linearly with the reciprocal of temperature from 3.8 to 58 K. Nonlinear behavior might be expected if the singlet were below a nearby triplet state of the carbene.

Irradiation of BDAF in MTHF at 77 K generates a meta-stable species with apparent absorption maxima at 485, 459, and 434 nm (Figure 2A). Warming the frozen glass to room temperature and then recooling to 77 K destroys the species responsible for these absorptions.

Comparison of the results from the electron resonance spectroscopy with those from optical measurements points to assignment of one or more of the absorption bands between 485 and 434 nm to BFL. This assignment cannot be made with certainty from the available data, but it is strongly supported by the results of some picosecond and nanosecond experiments described below.

(2) Transient Absorption Spectroscopic Analysis of BDAF. Irradiation of a 2 × 10⁻⁴ M solution of BDAF in cyclohexane at room temperature with the frequency-tripled output of a mode-locked Nd-YAG laser (ca. 30 ps, 355 nm, 4 mJ) generates a transient product detected by its optical absorption spectrum. This spectrum exhibits a maximum at ca. 450 nm which is fully present in less than 50 ps (Figure 2B). On a longer time scale, the transient product decays following first-order kinetics (t₁/₂ = 280 ps). Weakly absorbing products from the reaction of the 450-nm transient are detected between 480 and 500 nm in this experiment and in a related nanosecond (15 ns, 337 nm, 7 mJ) time scale photolysis. These findings are summarized in eq 2. Similar results are obtained when the photolysis of BDAF is carried out in perdeuteriocyclohexane (C₆D₁₂).

\[
\text{BDAF} \quad \text{hv}, \text{C}_6\text{H}_5 \quad \text{"450nm"} \quad \text{<50ps} \quad \text{Products (2)}
\]

Irradiation of BDAF in acetonitrile solution also leads to the generation of transient intermediates. In this solvent the transient absorbs at ca. 460 nm and is formed in less than 100 ps. The lifetime of the transient in this case is greater than 100 ps. The lifetime of the transient in this case is greater than 100 ps. Its decay obeys first-order kinetics and a second absorption appears in the spectrum as the first disappears. This second species has an absorption maximum at ca. 520 nm and is stable indefinitely. The final spectrum in this experiment is quite similar to that of the carbene dimer (bis(2,3-benzofluorenylidene)) reported previously. The lifetime of the first transient and the yield of presumed carbene dimer depend on the BDAF concentration (t₁/₂ = 62 ns, 7 × 10⁴ M). The lifetime of the transient product absorbing at 460 nm is independent of the laser power, and the changes in absorbance both at 460 and 520 nm vary linearly with the power. Also, the species absorbing at 520 nm does not react with dimethyl fumurate, a reagent known to combine rapidly with the nitrile ylide formed from FL and acetonitrile. Comparable results are obtained when the irradiation of BDAF in benzene solution is monitored spectroscopically.

(3) Chemical and Kinetic Behavior of Benzo-fluorenylidene. The irradiation of BDAF in cyclohexane at room temperature gives benzofluorene (BFH₂), 11-cyclohexylbenzofluorene (CYBF), and dihydrobis(benzofluorenylidene) (BFB) in a ratio of ca. 1:11:4 (eq 3). When

\[
\text{BDAF} \quad \text{hv} \quad \text{C}_6\text{H}_5 \quad \text{BFH}_2
\]

the irradiation of BDAF is carried out in a 1:1 mixture of C₆H₆ and C₆D₁₂, the mass spectrum of the 11-cyclohexylbenzofluorene shows no measurable formation of a singly deuterated component. In contrast, the BFB formed in this reaction is a mixture of d₄, d₅ compounds (74:26). These findings, together with the picosecond absorption spectroscopy, indicate that BFL reacts with cyclohexane to form CYBF primarily by direct insertion into a carbon-hydrogen bond rather than by a two-step abstraction recombination sequence proceeding through free radicals. Direct insertion reactions of this type are usually associated with the chemistry of singlet carbones. The formation of BFB, on the other hand, must involve combination of free 11-benzofluorenyl radicals (BFLH) to account for the isotope distribution.

(10) This finding is consistent with related results from other laboratories; see ref 3 and 6.
Irradiation of BDAF in benzene containing 2.5 M methyl alcohol gives methyl 11-benzofluorenyl ether (MBFE) in 80% yield. Analysis of this reaction by nanosecond transient absorption spectroscopy shows that the lifetime of the intermediate absorbing at 460 nm decreases as the concentration of methyl alcohol in the solution increases (Figure 3). Least-squares analysis of these data reveals that the transient product appears to react with methanol with a bimolecular rate constant \( k_{OM} \) equal to \( 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \). Exactly analogous results are obtained when the rate of this reaction is measured in acetonitrile solvent \( k_{OM} \text{CH-CN} = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \). Formation of an ether from reaction of a carbene with an alcohol has generally been a process associated with the singlet state of the carbene.

Photolysis of BDAF in benzene containing 0.7 M \( \alpha \)-methylstyrene gives the appropriate cyclopropanes (a mixture of regioisomers) in ca. 90% yield. The laser spectroscopy shows that the transient product absorbing at 460 nm reacts with the styrene with a bimolecular rate constant \( k_{OM} \text{CH-CN} \) equal to \( 5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \). When \( (E)\)-\( \beta \)-deutério-\( \alpha \)-methylstyrene is used, the NMR spectrum of the isolated cyclopropanes shows that they are formed with retention of 80% of the stereochemistry of the starting olefin.

We conducted a classical competition experiment to confirm that the rate constants measured for the reactions of the transient product with methanol and with \( \alpha \)-methylstyrene correspond to the actual formation of the observed major products. Irradiation of an acetonitrile solution of BDAF containing 0.049 M methyl alcohol and 0.69 M \( \alpha \)-methylstyrene is anticipated to give the ether and the cyclopropane in a ratio of 1:0.20. The ratio observed with the \( ^1 \text{H} \) NMR spectrum of the mixture is within experimental error of the expected value.

The direct photolysis of BDAF presumably generates singlet benzofluorenylidene, which in turn intersystem crosses to its triplet ground state. Triplet sensitization, on the other hand, is expected to give triplet benzofluorenylidene without first forming the singlet carbene. We examined the triplet benzil sensitized reactions of BDAF with methyl alcohol, \( (E)\)-\( \beta \)-deutério-\( \alpha \)-methylstyrene, and a 1:1 mixture of \( \text{C}_6\text{H}_{12} \) and \( \text{C}_8\text{D}_{12} \).

BDAF quenches the phosphorescence of benzil. Irradiation (424 nm) of benzil (3.5 \( \times \) 10\(^{-2} \) M) in the presence of BDAF leads to the consumption of the diazo compound. This reaction is appropriately slowed when anthracene, a specific quencher of benzil triplet, is included in the reaction solution. This observation confirms the triplet sensitization.

Triplet benzil sensitized decomposition of BDAF in benzene containing 2.5 M methyl alcohol gives the ether (MBFE) in 92% yield. This result indicates that the carbene spin state required for ether formation can be formed either by direct irradiation, which presumably generates \( 1 \)-BFL initially, or by triplet sensitization, which is expected to give \( 3 \)-BFL first. Similarly, the stereochemical outcome of the cyclopropanation of \( \alpha \)-methylstyrene is the same for the triplet sensitization as it is in the direct irradiation. Finally, the deuterium incorporation in CYBF is the same for triplet sensitization of BDAF in a mixture of \( \text{C}_6\text{H}_{12} \) and \( \text{C}_8\text{D}_{12} \) as it is for the direct irradiation.

### Discussion

The chemical and physical properties of BFL are closely related to those of FL. There are some notable differences however (see Table I), and these highlight the features that relate structure to reactivity for these aromatic carbones.

The laser spectroscopy reveals that the transient detected at 450 nm is consumed very rapidly in cyclohexane solution. The products in this case indicate that the dominant mechanism of this transformation is direct insertion into a carbon–hydrogen bond of the solvent accompanied by a smaller contribution from an abstraction–recombination sequence that goes through free benzofluorenyl radicals. This conclusion is supported also by the absence of strong transient absorptions due to BFL sensitized irradiation of BDAF in cyclohexane. Direct insertion is generally thought to be a singlet carbene reaction. However, the low-temperature EPR spectroscopy indicates that the ground state of BFL is the triplet carbene.

The formation of an ether from reaction of a carbene with an alcohol has generally been attributed exclusively to reaction of the singlet spin state. This spin-selective reactivity is directly supported by the observation that triplet boraanthrylidene (BA), formed by sensitization, does not give ethers from alcohols. It has recently been suggested that triplet diphenylmethylene can react in one step with methyl alcohol to give the appropriate ether.

### Table I. A Comparison of Fluorenylidene and Benzofluorenylidene

<table>
<thead>
<tr>
<th>FL</th>
<th>BFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{OM} \text{CH-CN} )</td>
<td>( 8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( k_{OM} \text{CH-CN} )</td>
<td>( 3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( k_{OM} \text{CH-CN} )</td>
<td>( 2.5 \times 10^8 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( \Delta G_{TS} )</td>
<td>( 1.9 \text{ kcal/mol} )</td>
</tr>
</tbody>
</table>

*Rate of formation of transient identified as the carbene.

(18) This represents a minimum yield since the ether is unstable to secondary photolysis: Tomlina, H. J. Chem. Soc., Chem. Commun. 1983, 1070.


It is instructive to compare our estimates of $\Delta G_{ST}$ for FL and BFL with the theory developed by Gleiter and Hoffmann.\(^{(24)}\) The similar geometry at the carbene carbon, indicated by the EPR spectra, eliminates one variable (the carbene-carbon bond angle) they identify as controlling $\Delta G_{ST}$ for methylene. The other important variables are the availability, occupancy, and energy of an orbital of proper symmetry for mixing with the \(p\)-type nonbonding carbene orbital.\(^{(24)}\) For FL and BFL the aromatic \(\pi\)-system contains orbitals of proper symmetry for this mixing. One clear difference between FL and BFL is the relative energies of the occupied and unoccupied aromatic orbitals that mix with the carbene \(p\) orbital. The energy of singlet BFL is predicted to be lowered relative to the triplet by this mixing more than for FL. Just this effect is observed. The results show that the singlet–triplet gap of BFL is about one half of what it is for FL. These considerations can be used to understand the factors controlling the chemical and physical properties of all of the aromatic carbenes that have been studied.\(^{(23)}\) This analysis is discussed in more detail in the related papers on bis(methoxy)fluorenylelidene and xanthylidene.\(^{(21)}\)

### Experimental Section

**General Procedures.** Proton magnetic resonance \((^1\text{H} \text{ NMR})\) spectra were recorded on Varian Associates XL-200 (200 MHz) or HR220 (220 MHz) spectrometers operated in FT mode in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard. Mass spectra were obtained with Finnigan-MAT 731 and CH5-DF mass spectrometers. Steady-state ultraviolet–visible (UV–vis) absorption spectra were recorded with a Perkin-Elmer Model 552 or Model Lambda 3 or Cary 14 spectrophotometer. Electron paramagnetic resonance (EPR) were recorded on a Varian Associates E-4 or Bruker X-band spectrometer equipped with an Oxford helium flow cryostat. Signal intensity is reported in arbitrary units. Elemental analyses were performed by the Analysis Laboratory, University of Illinois. The nanosecond and picosecond laser equipment has been described previously.\(^{(26)}\)

**Materials.** Acetonitrile (Aldrich Gold Label) was refluxed for 4–6 h over CaH\(_2\) and distilled under nitrogen. 2-Methyltetrahydrofurane (Aldrich) was passed through a column of freshly activated neutral alumina (Wolém, activity grade 1). All other solvents are commercially available and were used as received.

BDAF was prepared by oxidation of the corresponding hydrazone with use of either mercuric or silver oxide. The resulting solid was recrystallized from hexane or petroleum ether, giving red crystals, mp 138 °C. Anal. Caled for C\(_{17}\)H\(_{10}\)N\(_2\): C, 84.28; H, 4.65; N, 11.56. Found: C, 84.39; H, 4.26; N, 11.58.

**Irradiation of BDAF in Cyclohexane.** A solution of BDAF (2.4 M \(\text{C}_6\text{H}_{12}\)) in cyclohexane (20 mL) was degassed with N\(_2\) and irradiated in a Rayonet photoreactor with 350-nm lamps. After irradiation the solvent was evaporated under vacuum and the residue analyzed by \(^1\text{H} \text{NMR} \) and GC/MS spectroscopy. The GC trace (3 ft, 5% OV-101 on Chromosorb W, column temperature 180–290 °C, 10 °C/min) shows four components with areas in the ratio of \(1:4:11:4\). Analysis of the mass spectrum of the minor component (retention time 2.59 min) reveals it to be 2,3-benzofluorenone. The second component (retention time 4.27 min) is 11-benzofluorenone. The major component (retention time 7.36 min) is 11-cyclohexylbenzofluorene (CYBFL); MS (70 eV), \(m/e\) (relative abundance) 298 (23), 216 (62), 215 (100); molecular ion calcd for C\(_{23}\)H\(_{22}\)O\(_2\)N: 312, 298, 215, 214 (100); molecular ion calcd for C\(_{24}\)H\(_{22}\)O\(_2\)N: 328, 314, 298 (100).

The \(^1\text{H} \text{NMR} \) spectrum of the reaction mixture shows a doublet at 5.41 characteristic of CYBFL and a singlet at 6.51 characteristic of BFL.

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The singlet at δ 4.09 characteristic of BFLH₂ cannot be detected. In a similar experiment, BDAF was irradiated in a 1:1 (V/V) mixture of C₆H₅Cl and C₂H₅Cl. The reaction mixture was analyzed by FI mass spectroscopy for incorporation of deuterium. The 2,3-benzofluorene was 9% monodeuterated, the CYBDF derived from C₆H₅Cl showed no significant deuterium incorporation and the dimer BBF was 26% monodeuterated.

Irradiation of BDAF in Benzene Containing Methanol. A solution of BDAF (1.3 mg, 5.3×10⁻³ mmol) in benzene (5 mL) containing methyl alcohol (2.5 M) was purged with N₂ and irradiated at 424 nm through an interference filter. When the reaction was complete (UV), the solvent and unreacted alcohol were removed under vacuum. The 'H NMR spectrum of the residue showed it to be a mixture of isomeric cyclopropanes formed in essentially quantitative yield as indicated by integration against p-dioxane as a standard; ¹H NMR (CDCl₃) δ 2.45 (t, 1 H), 2.1 (q, 1 H), 1.75 (d, 3 H), 7.2-8.6 (m, 15 H); MS (70 eV), m/e (relative abundance) 332 (53), 255 (6), 215 (51); molecular ion calcd for C₁₉H₁₄O m/e 332.1565, found 332.1570.

In an analogous experiment, (E)-β-deuterio-α-methylstyrene (1.76 M) was used and the stereochemistry of the cyclopropanation reaction was determined by ¹H NMR spectroscopy to be 77 ± 13% retention.

Triplet-Sensitized Photolysis of BDAF in CH₃CN Containing α-Methylstyrene. An acetonitrile solution (10 mL) of BDAF (2.0×10⁻³ M), α-methylstyrene (0.73 M) and benzil (6.6×10⁻³ M) was purged with N₂ and irradiated through a 424-nm interference filter. The solvent and unreacted styrene were removed under vacuum. The 'H NMR spectrum of the residue revealed formation of the expected cyclopropane in greater than 85% yield.

In an analogous experiment, (E)-β-deuterio-α-methylstyrene (0.70 M) was used. The stereochemistry of the cyclopropanation reaction was found to be the same as in the direct irradiation. Control experiments showed that benzil is not quenched significantly by the styrene at the concentrations used and that the styrene is not significantly isomerized under these conditions.

Acknowledgment. This work was supported by grants from the National Science Foundation and from the National Institutes of Health. Some of these results are taken from the Ph.D. thesis of B. Brauer, University of Illinois, 1984. We thank Dr. P. DeBrunner for his help with the low-temperature EPR spectroscopy.

Total Synthesis of (+)-Pipoxide and (+)-β-Senepoxide and Their Diene Precursors

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(2R)-trans-2,3-Diacetoxy-1-[(benzyloxy)methyl]cyclohexa-4,6-diene (6), a diene precursor in the biosynthesis of highly oxygenated cyclohexene epoxides, has first been totally synthesized from the bromo lactone 16 derived from (1S)-endo-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (18), adopting the procedure formerly used for the synthesis of racemic 6. Chemical conversions of 6 into the other dienes (10 and 13) and epoxides, (+)-pipoxide (4) and (+)-β-senepoxide (5), have also been achieved. The present syntheses constitute formal total synthesis of (+)-pipoxide (2), (−)-tintanoxide (3), and (−)-zeylenoal (14).

The plant metabolites (+)-croteoxide (1), (−)-senepoxide (2), (+)-pipoxide (4), and (+)-β-senepoxide (5) belong to a family of highly oxygenated cyclohexene epoxides exhibiting interesting biological activity. Recent extensive work on plants in the Uvaria genus has led to the discovery of intermediate, the “missing link”, dienes 6, 10, and 13, which are key substances for elucidation of the biogenesis of the compounds of this class, and further added two new epoxides, (−)-tintanoxide (3) and (+)-β-senepoxide (5), to the Uvaria genus. 

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