RESEARCH ARTICLE

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Photochemical generation of 9-Fluorenyl radicals

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Abstract

A series of 9*H*-fluorenols and 9*H*, 9'H-bifluorenyls were irradiated in less polar solvents giving photoproducts derived from their corresponding 9*H*-fluorenyl radicals. These transient species were directly observed by laser flash photolysis and their UV/visible spectra compared with those of their corresponding cations. Theoretical calculations (density functional theory [DFT]) of these intermediates indicate their destabilizing nature in similar fashion to the antiaromatic character of the corresponding cations.

KEYWORDS

fluorenols, bifluorenyls, fluorenyl radicals, laser flash photolysis, fluorenyl cations, computational studies, aromatic stabilization, resonance stabilization energy

1 | INTRODUCTION

Ever since the first characterization of a persistent carboncentered radical in 1900,^[1] the importance of these ubiquitous species in atmospheric chemistry,^[2] combustion,^[2] polymerization,^[3] and biology^[4] has been well recognized. The inherent uncharged nature of these species renders them susceptible to bimolecular reactions such as hydrogen atom abstraction and additions to multiple bonds and C-C bond formation such as dimerization. Their open-shell electronic configuration also make these prone to reactions with ground state (triplet) molecular oxygen with formation of peroxides and subsequent autoxidation accounting for their transient nature under aerobic conditions. In spite of their transitory nature, these species have been utilized in organic synthesis through their selective C-C bond forming reactions.^[5] The electron-deficient nature of these open shell intermediates permits facile additions to alkenes and alkynes resulting in C-C bond formation.^{5c} Furthermore, substituent effects on the relative stabilizations of these neutral species parallel those for their carbocation analogues.^[6]

Our interests in carbocations incorporated into destabilizing electronic environments such as bonding to electron-deficient moieties or as part of an antiaromatic cyclic configuration, such as cyclopentadienyl,^[7] prompted the current studies of their radical analogues.^[8] The 9-fluorenyl cation can be formally regarded as an antiaromatic carbocation possessing the 12π cyclic electronic configuration. The 9-substituted carbocations can be generated by photolysis of their alcohol precursors in highly solvating polar medium. For example, irradiation of 9H-fluorenols in polar solvating solvents such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) or 1,1,1-trifluoroethanol (TFE) results in formation of the corresponding carbocation intermediates.^[7] By contrast, photolysis of these substrates in less polar solvents gives products which are formally derived from their radical intermediates (Scheme 1). One of the principal products obtained is the corresponding 9H, 9'H-bifluorenyl formally derived from coupling of the radical intermediate. We observed that these dimers are themselves photolabile and reversibly form the corresponding 9-fluorenyl radicals under the irradiation conditions. To our knowledge, no



SCHEME 1 Irradiation of Cyanobifluorenyls 3d and 3e

systematic study of the photochemistry of 9,9'-bifluorenyls as a source of these radicals has been reported.

2 | EXPERIMENTAL

2.1 | Apparatus and reagents

All reactions were carried out in dried glassware. Proton spectra were obtained on Bruker ARX-400, ARX-300, or ARX-600 spectrometers. Solutions in 99.8% CDCl₃ with 1% tetramethylsilane (TMS) as internal standard were used. Photolyses were performed using a Hanovia 450 W medium pressure mercury arc lamp in a quartz immersion well. All solutions were purged with argon prior to irradiation. Melting points of all compounds were determined on a Reichert melting point apparatus and are uncorrected. 9-Trifluoromethylfluorenol,^[9] 9,9'-bifluorenyl,^[10] 9,9'-bistrifluoromethyl-9,9'-bifluorenyl,^[8] 9,9'-dicyano-9,9'bifluorenyl,^[11] and 9-cyano-9,9' bifluorenyl^[12] were prepared by literature procedures.

2.2 | Irradiation of 9,9'-dicyano-9,9'bifluorenyl (3d)

A solution containing 40 mg (0.105 mmol) of dicyanobifluorenyl **3d** in 80 mL of methanol was irradiated for 2 hours. Removal of the solvent under vacuum followed by chromatographic purification (7% ethyl acetate-hexane) yielded 4 mg (11.5%) of 9H-fluorene **2a**, 3 mg (7.9%) of fluoren-9-one, 8 mg (20%) of 9-cyanofluorene **2d**, 3 mg (7.3%) of 9-methoxyfluorene, 4 mg (11.5%) of 9,9'-bifluorenyl **3a**, and 5 mg (12.5%) of unreacted **3d**. The characterization of each product was based on comparison of physical and spectral data with those of authentic samples.

2.3 | Irradiation of 9-cyano-9,9'bifluorenyl(3e)

A solution of 9,9'-bifluorenyl **3e** (50 mg, 0.14 mmol) in methanol (20 mL) was irradiated for 15 minutes. Evaporation of the solvent under vacuum followed by chromatographic purification (7% ethyl acetate-hexane) yielded 6 mg (13%) of 9H-fluorene **2a**, 3 mg (6%) of fluoren-9-one, 3 mg (5.7%) of 9,9'-dicyano-9,9'-bifluorenyl (**3d**), 8 mg (17.4%) of 9,9'-bifluorenyl **3a**, and 4 mg (8%) of unreacted starting material **3e**. Characterization of the photoproducts was based on comparison with authentic samples.

2.4 | Irradiation of 9-cyanofluorene (2d)

A solution of 9-cyanofluorene **2d** (35 mg, 0.183 mmol) in methanol (25 mL) was irradiated for 1 hour. Evaporation of the solvent under vacuum followed by chromatographic purification (7% ethyl acetate-hexane) yielded 4 mg (13.3%) of 9H-fluorene **2a**, 3 mg (9.1%) of fluoren-9-one, 4 mg (13.3%) of 9,9'-bifluorenyl **3a**, 2 mg (5.5%) of 9-methoxyfluorene, and 13 mg (37.1%) of recovered **2d**.

2.5 | Laser flash photolysis

Excitation wavelength for these experiments is 248 nm. A KrF excimer laser (248 nm, ~25 ns, 94-102 mJ/pulse) was used and deoxygenated solutions of methanol or hexanes as solvent were analyzed. Transient spectra were recorded using a flow system.^[13]

2.6 | Computational studies

Geometries were optimized, and energies were calculated, using density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional and a "cc-pVTZ" basis set (correlation-consistent triple zeta plus polarization). B3LYP is a good general purpose functional, and by far the most popular for calculations of equilibrium geometries and energies of molecules of main group elements.^[14] The cc-pVTZ is a standard diffuse basis set that gives medium to high accuracy on valence excitations.^[15] Vibrational frequencies were calculated for each minimum energy structure to verify that the structures found were indeed equilibrium geometries and to get zero-point energies (ZPEs). The bond dissociation energies, BDEs, were calculated by taking differences of free energies, which include the ZPE and thermal corrections calculated at room temperature. Excitation

energies were calculated in vacuum, and in methanol using the polarizable continuum model (PCM).^[16]

3 | **RESULTS AND DISCUSSION**

3.1 | Photoproducts from 9-Fluorenols and 9,9'-Bifluorenyls in methanol

We reported recently^[8] on the photochemistry of a series of 9H-fluorenols 1a-c giving the reduced fluorenes 2a-c and 9,9'-bifluorenyls 3a-c as principal products. Evidence for the intermediacy of 9-fluorenyl radicals was the trapping of the transient with TEMPO in the case of the parent 9*H*-fluorenol (**1a**).^[8] The 9,9'-bifluorenyls (**3a-c**) undergo photoexcitation to give the reduced fluorenes in hydrogen-donating solvents including methanol, indicative of homolysis of the benzylic C-C bond. In one instance, the photolysis of 3c led to isomerization to the bifluorenyl 4c in alcohols and other polar solvents. In order to probe the mechanism of this unprecedented transformation, these studies were extended to the electron-withdrawing cyano substituted bifluorenyl 3d. Furthermore, the presence and nature of the fluorenyl radical intermediates was probed by laser flash photolysis of 9-fluorenols 1 and 9,9'-bifluorenyls 3. The relative stabilities of these intermediates were assessed using theoretical calculations and compared with their corresponding antiaromatic carbocations.



3.2 | Photoproduct distribution from continuous irradiation of cyano substituted bifluorenyls

Continuous irradiation of methanolic solutions of bifluorenyls **3d** and **3e** gives rise to products formally

derived from 9-cyanofluorenyl radical leading to the reduced 9-cyanofluorene (2d) or coupling to the bifluorenyl 3d as is evident from the photolysis of the unsymmetrical compound 3e (Scheme 1). The latter substrate appears to dissociate into both the 9-cyanofluorenyl and fluorenyl radicals as evident from formation of both bifluorenyls 3d and 3a. The intermediacy of both radicals is shown from the transient spectra obtained from flash photolysis of 3e (vide infra). Furthermore, 9-cyanofluorene was found to be photolabile, and independent experiments have shown that it is transformed to fluorene and bifluorenyl under the irradiation conditions. Small amounts of fluorenone and 9-methoxyfluorene were also observed and attributed to incomplete deoxygenation purging, and solvent nucleophilic quenching of the carbocation formed in competition.

3.3 | Time resolved spectroscopy

Laser flash excitation at 248 nm of fluorenols 1a and 1c, and bifluorenyls 3a, 3c, 3d, and 3e generated transients which exhibit UV/visible spectra characterized by bands in the 500-540 nm wavelength region (Figure 1). These transients decay by second order kinetics with rate coefficients 2 $k/\varepsilon_{\lambda max} \sim 0.3-2.1 \times 10^7 \text{cm s}^{-1}$ in deoxygenated solutions. The lifetimes decrease with increasing oxygen atmosphere indicative of radical species. The similarity of the transient spectra generated from fluorenols 1a and 1c with the corresponding bifluorenyls 3a and 3c, respectively, suggests that these transients are associated with the fluorenyl radicals derived from C-O and C-C bond homolysis, respectively. The radicals exhibit peaks that are similar to their corresponding carbocations^[7] except that the latter peaks are slightly red-shifted (15 nm for R = H, 20 nm for $R = CF_3$). The peaks observed below 400 nm decay more slowly and are likely associated with the triplet state of the substrates.

The transient spectrum obtained from irradiation of **3e** shows two species in the low energy region as evident from the overlapping peaks at 500-540 nm with the slower decaying transient at 540 nm corresponding to the 9-cyanofluorenyl radical. This value is consistent with that reported for the 9-cyanofluorenyl radical.^[17] The bathochromic shift seen for the 9-substituted fluorenyl radicals bearing electron-withdrawing groups, CF₃ and CN, is corroborated by theoretical calculations (Table 1) even though the absolute values are in discrepancy due to nonaccountability of solvation effects in the theoretical model. The bathochromic shifts are associated with the greater spin density delocalization for the radicals and charge delocalization for the



FIGURE 1 LFP data (248 nm excitation in argon purged methanol solutions)

| TABLE 1 | Theoretical and experimental low energy transition |
|-------------|--|
| absorptions | for Fluorenyl radicals |

| R | λ _{simulated in} _{vacuum} (nm) | λ _{exp. obs.} (nm) | λ _{simulated in} _{MeOH} (nm) |
|-----------------|---|--------------------------------|---|
| н | 450 | 500 | 451 |
| CH ₃ | 430 | - | 425 |
| CF ₃ | 485 | 530 | 495 |
| CN | 490 | 540 | 515 |

carbocations with electron-withdrawing substituents. Theoretical calculations to include methanol solvation effects also show bathochromic shifts closer to the experimental values for the fluorenyl radicals bearing electron-withdrawing groups, CF₃ and CN.

3.4 | Kinetic and thermodynamic stabilities of 9-Fluorenyls

As can be seen from the second order rate constants for the transient decay profiles, the parent 9-fluorenyl decays faster $(1.6-2.1 \times 10^7 \text{ cm s}^{-1})$ than the 9substituted CN and CF₃ analogues by a factor of 4 to 5 (Figure 1), assuming that the extinction coefficients for these compounds are the same. This observation is consistent with the data reported by Scaiano^[17] for the relative reactivity of 9-fluorenyl and 9-cyano-9-fluorenyl radicals toward oxygen quenching, which is rationalized in terms of electronic factors associated with spin delocalization of the unpaired electron into CN. The case for the lower reactivity of 9-CF₃ substituted fluorenyl compared with parent fluorenyl radical may be due to



 $\Delta G = RSE (kcal mol^{-1})$

TABLE 2 Free energy difference of Fluorenyl C-H bond dissoci-
ation and for the reaction in Scheme 2 (kcal Mol^{-1})

| R | 9H-Fluorene (ΔG) | 9,10-Dihydroanthracene (ΔG) | (ΔG _{rxn}) |
|-----------------|---------------------|--------------------------------|----------------------|
| н | 76.4 | 71.2 | -5.2 |
| CH ₃ | 72.1 | 72.0 | -0.1 |
| CF ₃ | 77.4 | 78.2 | +1.2 |
| CN | 67.0 | 63.7 | -3.3 |

steric factors. The relative thermodynamic stabilities of 9-substituted fluorenyl radicals may be computed by comparison of the C-H bond dissociation energies of the C(9)-H bond of fluorene with that of the benzylic C-H bond of the nonaromatic dihydroanthracene according to Scheme 2. The computed values are tabulated in Table 2.

As can be seen, the fluorenyls are all destabilized relative to the nonaromatic model except for 9-CF₃. Of note is the nonplanarity of the comparative model system (dihydroanthracene) relative to fluorenyl, which diminishes the extent of electron delocalization into the benzene ring of the former. The relative free energy difference values point to an inherent destabilization of fluorenyls. In regard to the 9-CF₃ substituted fluorenyl, the strong electron-withdrawing substituent may induce greater spin delocalization into the conjugated benzene rings, which can be better accommodated in the more planar fluorene ring than the model system. This observation can also account for the unusual formation of 4c $(\mathbf{R} = \mathbf{CF}_3)$ on photoexcitation of either 1c or 3c where the corresponding fluorenyl radical has been shown to be directly involved in product formation. The spin density of this radical is predominantly localized at C-1 and C-3 (0.156). With the peri-steric effect recombination of the fluorenyl radicals takes place selectively at C-3 accounting for the regiochemistry of the product. It is interesting to note that no evidence of a similar photoproduct is observed in the photolysis of bifluorenyls 3d and 3e, which also has an electron-withdrawing CN group. The 9-cyanofluorenyl radical has most of the spin-density localized on the nitrogen atom rather than at C-3.

4 | CONCLUSIONS

In summary, photoexcitation of 9,9'-bifluorenyls generates the corresponding fluorenyl radicals in methanol solutions as evident from the laser flash photolysis of both bifluorenyls and the corresponding fluorenols. These transients show peaks in the region λ 500-540 nm and decay by second order kinetics. Their spectral features are similar to the corresponding carbocations, with the latter showing red shifts of 15-20 nm. These radicals can undergo hydrogen abstraction from solvent to produce the reduced 9-substituted fluorenes, or dimerize to the bifluorenyls as was evident from the photolysis of monosubstituted bifluorenvl 3e, which results in both fluorenyl and 9-cyanofluorenyl radicals. Computed resonance stabilization energies indicate an inherent destabilization of fluorenyl radicals except for the 9-CF₃ analogue, which is rationalized in terms of delocalization of spin density into the planar benzene rings. This also accounts for the formation of the unusual dimerization to the unsymmetrical bifluorenyl 4c. Whereas the fluorenyl radicals are destabilized (except for 9-trifluoromethylfluorenyl) relative to their nonaromatic analogues, their kinetic stabilities increase with substitution at C-9 due to stereoelectronic factors.

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