Transient Resonance Raman and Density Functional Theory Investigation of the 2-Fluorenylnitrenium Ion

Peizhi Zhu, Shing Yau Ong, Pik Ying Chan, King Hung Leung, and David Lee Phillips*

Contribution from the Department of Chemistry, The University of Hong Kong,
Pokfulam Road, Hong Kong S. A. R., P. R. China

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Abstract: We report a transient resonance Raman spectrum for the 2-fluorenylnitrenium ion obtained after photolysis of 2-azidofluorene. The 10 experimental Raman band frequencies of the transient spectrum show very good agreement with the computed frequencies from BPW91/cc-PVDZ density functional theory calculations for the 2-fluorenylnitrenium ion. Our results confirm the assignment of the ∼460 nm transient absorption band formed after photolysis of 2-azidofluorene in water/acetonitrile or water solution to the singlet ground electronic state 2-fluorenylnitrenium ion. Our study indicates the 2-fluorenylnitrenium has a large degree of iminocyclohexadienyl cation character with significant delocalization of the charge over both phenyl rings of the fluorene moiety. We compare our results for the 2-fluoreneylnitrenium ion to those previously reported for several other arylnitrenium ions.

Introduction

Since arylnitrenium ions are suspected to play a key role in chemical carcinogenesis, there is a great deal of interest in their properties and chemical reactions.[1−18] Some aromatic amines such as 2-acetylaminofluorene are enzymatically transformed into sulfate esters of the analogous *N*-hydroxylamines and in aqueous environments a sulfate anion will spontaneously leave these esters to form an arylnitrenium ion.[13,17] Some arylnitrenium ions (such as the 2-fluorenylnitrenium ion) can be selectively trapped by guanine bases in DNA[8−10,14,18] and this is believed to result in carcinogenic mutations.[15] Transient absorption spectroscopy has recently been used to characterize the reaction of the 2-fluorenylnitrenium ion with 2′-deoxyguanosine and a new reaction intermediate was observed on the way to form the 8-(2-fluorenylamino)-2′-deoxyguanosine adduct.[18]

Arylnitrenium ions are typically short-lived and difficult to study in room temperature solutions. Several groups have recently produced arylnitrenium ions using photochemical methods and this has enabled more general spectroscopic characterization of arylnitrenium ions.[19−30] A number of nitrenium ions have been characterized by transient absorption spectroscopy experiments and a good deal has been learned about arylnitrenium ion lifetimes and rate constants for reactions with other species.[18−30] However, there are few direct experimental measurements of the structure and bonding of these short-lived arylnitrenium ions. Time-resolved infrared absorption spectroscopy (TRIR) experiments have recently been used to obtain vibrational spectra of several nitrenium ions.[28,31] The first

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* Author to whom correspondence should be addressed.

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such study confirmed that the diphenylnitrenium ion has an iminocyclohexadienyl cation-like structure.[28] A very recent investigation used TRIR to characterize substituent effects on the symmetrical aromatic C═C stretch mode(s) in the 1580−1628 $\mathrm{cm^{-1}}$ region for four *N*-methyl-*N*-phenylnitrenium ions.[31] The experimental vibrational frequencies were found to have excellent agreement with values computed from BPW91/cc-PVDZ density functional theory calculations. The computational results exhibited noticeable bond length alternation in the phenyl rings accompanied by smaller C−N bond lengths and significant positive charge delocalization into the phenyl rings.[31]

In this paper we report a preliminary transient resonance Raman investigation of the 2-fluorenylnitrenium ion produced from photolysis of a 2-azidofluorene precursor in a 75%water/25%acetonitrile by volume mixed solvent. To our knowledge, this is the first transient vibrational spectrum reported for the 2-fluorenylnitrenium ion and the first transient resonance Raman spectrum for an arylnitrenium ion formed via a photochemical reaction. We also note that this is the first transient vibrational spectrum obtained for a photochemically produced arylnitrenium ion in a largely aqueous system. We observe a resonance Raman spectrum that contains a number of fundamental bands in the 1100−1700 $\mathrm{cm^{-1}}$ region as well as several combination bands in the 2400−3300 $\mathrm{cm^{-1}}$ region. These Raman vibrational frequencies show very good agreement with those computed from BPW91/cc-PVDZ density functional calculations for the 2-fluorenylnitrenium ion. Our results confirm the assignment of the ∼460 nm transient absorption band to a singlet 2-fluorenylnitrenium species. Our transient resonance Raman and BPW91/cc-PVDZ computational results indicate the 2-fluorenylnitrenium ion has substantial iminocyclohexadienyl character with significant carbon−carbon bond alternation in both phenyl rings. We compare our results for the 2-fluorenylnitrenium ion to results for several other arylnitrenium ions.

Experimental and Computational Details

The 2-azidofluorene sample was synthesized according to the literature method (further details of the synthesis are given in the Supporting Information).[18,29,32] Samples of the 2-azidofluorene precursor were prepared with concentrations of ∼5 mM in a 75% water/25% acetonitrile (spectroscopic grade) by a volume mixed solvent system with a 2 mM acetate buffer and a pH of 3.5. The transient resonance Raman spectra were obtained by using the experimental apparatus and methods previously described in refs 33−37 and only a brief description will be provided here. Hydrogen Raman shifted laser lines generated from the harmonics of a nanosecond pulsed Nd:YAG laser supplied the pump (309 nm) and probe (416 nm) beams for the transient resonance Raman experiments. Optical delays of 0−10 ns between the pump and probe pulses were used in the experiments. A near collinear geometry was employed to focus the pump and probe beams onto a flowing liquid stream of sample and the Raman scattering was collected with reflective optics and imaged through a polarization scrambler mounted on the entrance slit of a 0.5 m spectrograph. The grating of the spectrograph dispersed the Raman light onto a liquid nitrogen cooled CCD and the Raman signal was acquired by the CCD for ∼300 to 600 s before being read out to an interfaced PC computer. Approximately 10 to 20 of these readouts were accumulated to get a resonance Raman spectrum. Pump only, probe only, and pump−probe transient resonance Raman spectra as well as a background scan were obtained and the known Raman bands of the water/acetonitrile solvent were used to calibrate the wavenumber shifts of the resonance Raman spectra. The solvent and precursor 2-azidofluorene Raman bands were removed from the pump−probe transient resonance Raman spectrum by subtracting a probe only Raman spectrum. The pump only spectrum was also subtracted from the pump−probe spectrum to get the transient resonance Raman spectrum of the photochemically generated 2-fluorenylnitrenium ion.

All of the density functional theory computations reported here made use of the Gaussian program suite.[38] Complete geometry optimization and vibrational frequency computations were done analytically by using the BPW91 method[39,40] with the cc-PVDZ basis set[41] for the ground electronic states of the 2-fluorenylnitrenium ion.

Results and Discussion

Flash photolysis of 4-azidobiphenyl or 2-azidofluorene in water/acetonitrile or water solvent leads to formation of intense broad characteristic transient absorption bands with a maximum at ∼460 nm that have been assigned to the 4-biphenylylnitrenium ion[21] and 2-fluorenylnitrenium ion,[18,21] respectively. These ions were observed to be fully present after the 20 ns laser pulse used in the transient absorption experiments and this implies they are formed with a rate constant of $>5 \times 10^7\ \mathrm{s^{-1}}$.[21] A recent picosecond measurement showed that the lifetime of the appearance of the 2-fluorenylnitrenium ion was about 100 ps.[25] We used a 309 nm pump laser wavelength (close to the 308 nm excitation wavelength used in the previous transient absorption study[21]) and a 416.0 nm probe wavelength (on the blue side of the broad ∼460 nm transient absorption band) for our transient resonance Raman experiments of 2-azidofluorene in a 75% water/25% acetonitrile solvent. Thus, our transient resonance Raman spectra should directly probe the identity and structure of the species responsible for the strong transient absorption band observed following ultraviolet photolysis of 2-azdiofluorene in water/acetonitrile solution. Figure 1 presents the 416 nm transient resonance Raman spectrum obtained following 309 nm excitation of 2-azidofluorene in 75% water/25% acetonitrile solution.

Table 1 lists the vibrational frequencies and tentative assignments for the resonance Raman bands observed in the transient Raman spectrum of Figure 1. Inspection of Figure 1 shows the transient Raman spectrum has a number of fundamental bands in the 1100−1700 $\mathrm{cm^{-1}}$ fingerprint region that also appear to have some combination bands in the 2500−3300 $\mathrm{cm^{-1}}$ region. Several reports have used time-resolved infrared absorption (TRIR) spectra and comparison to density functional theory computations to convincingly assign several arylnitrenium ions (biphenylylnitrenium ion[28] and four *N*-methyl-*N*-phenylnitrenium ions[31]) to their singlet ground electronic states. Therefore,

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Table 1. Experimental Raman Vibrational Frequencies Observed in the Transient Resonance Raman Spectrum in Figure 1[a]

vibrational mode	BPW91/cc-PVDZ calcd value (in cm^{-1})	transient resonance Raman freq shift (in cm^{-1})
ν_{34}, C−H bend	1013	
ν_{33}, C−H and N−H bend (in the plane)	1093	
ν_{32}, C−H and N−H bend (in the plane)	1109	
ν_{31}, C−H and N−H bend (in the plane)	1114	
ν_{30}, CH$_2$ twist	1123	
ν_{29}, CH$_2$ wag + C−H and N−H bending (in the plane)	1141	
ν_{28}, C−H bend	1155	
ν_{27}, CH$_2$ wag + C−H and N−H bend (in the plane)	1174	
ν_{26}, CH$_2$ wag + C−H and N−H bend (in the plane)	1187	
ν_{25}, C−CH$_2$ stretch + C−H + N−H bend (in the plane)	**1210**	**1204**
ν_{24}, C−CH$_2$ stretch + C−H and N−H bend (in the plane)	1282	
ν_{23}, C−CH$_2$ stretch + C−H and N−H bend (in the plane)	1323	
ν_{22}, CH$_2$ scissor + C−H and N−H bend (in the plane)	**1350**	**1346**
ν_{21}, CH$_2$ scissor + C−H and N−H bend (in the plane)	1370	
ν_{20}, N−H and C−N bending (in the plane)	**1378**	**1382**
ν_{19}, CH$_2$ wag + C−H and N−H bend (in the plane)	1393	
ν_{18}, CH$_2$ scissor + C−H and N−H bend (in the plane)	**1433**	**1431**
ν_{17}, C−H bend	**1469**	**1455**
ν_{16}, C−C stretch	**1482**	**1483**
ν_{15}, C−C stretch	1532	
ν_{14}, C−C stretch	**1557**	**1554**
ν_{13}, C−C stretch	**1561**	**1566**
ν_{12}, Ring 1 C−C stretch	**1607**	**1600**
ν_{11}, Ring 3 C−C stretch	**1640**	**1633**
$\nu_{20} + \nu_{25}$		**2595**
$\nu_{20} + \nu_{22}$		**2733**
$\nu_{16} + \nu_{22}/\nu_{11} + \nu_{25}$		**2837**
$\nu_{16} + \nu_{20}$		**2883**
$\nu_{11} + \nu_{20}$		**3026**
$\nu_{11} + \nu_{16}$		**3128**

[a] Tentative vibrational band assignments are also shown based on comparison to computed vibrational frequencies from BPW91/cc-PVDZ calculations in the 1000 to 1700 cm^{-1} fingerprint region for the ground singlet electronic state of the 2-fluorenylnitrenium ion (see text).

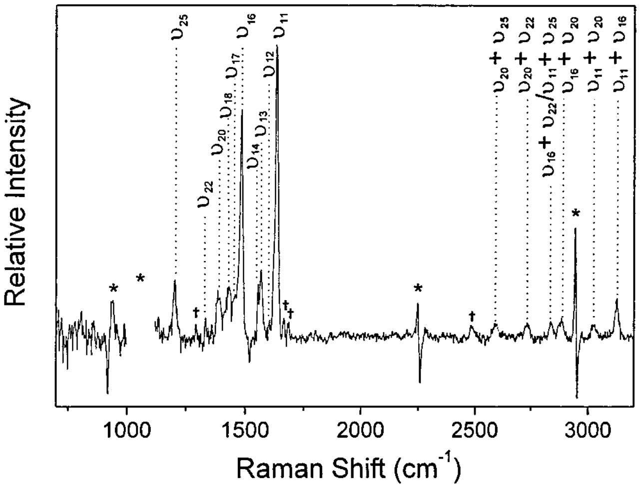

Figure 1. Transient 416 nm resonance Raman spectrum of the 2-fluorenylnitrenium ion formed after 309 nm photolysis of 2-azidofluorene in a 75% water/25% acetonitrile by volume mixed solvent. The transient resonance Raman spectrum was obtained by subtracting a probe only spectrum and a pump only spectrum from a pump−probe spectrum to remove solvent and precursor Raman bands. The region around 1000−1100 cm^{-1} marked by an asterisk is not shown due to a solvent subtraction artifact and the presence of a stray laser line. The other asterisks mark solvent subtraction artifacts and the daggers label small stray light or ambient light artifacts.

we expect that the 2-fluorenylnitrenium ion would likely be in its singlet ground electronic state and not the triplet ground electronic state. The most recent TRIR study found excellent agreement between the experimental vibrational frequencies and those values computed from BPW91/cc-PVDZ calculations.[31] We have performed similar BPW91/cc-PVDZ computations for the singlet ground electronic state of the 2-fluorenylnitrenium ion to find the optimized geometry and computed vibrational frequencies (see Supporting Information for a more complete listing than found in Tables 1 and 2). The experimental transient resonance Raman band vibrational frequencies in Table 1 display very good agreement with the computed BPW91/cc-PVDZ values (usually within 2 to 8 cm^{-1}) and serve as a good fingerprint for identification of the photoproduct species. Our results confirm that the singlet 2-fluorenylnitrenium ion is associated with the intense ∼460 nm transient absorption observed after photolysis of 2-azidofluorene in water/acetonitrile or water solutions. This is in agreement with the preliminary assignment of McClelland and co-workers.[18,21]

The transient resonance Raman spectrum in Figure 1 has most of its intensity in vibrational modes associated with the C=C stretches of the phenyl rings (in particular the ring with the N−H group attached) and the C−N−H group. Figure 2 presents a simple schematic of the normal mode descriptions for the vibrational modes in the 1200−1700 cm^{-1} region and the vibrational frequencies given in parentheses are those of the experimentally observed Raman bands. Inspection of Figure 2 shows that the normal mode descriptions are somewhat complex and contain contributions from a number of internal coordinates. Thus, it is instructive to use the predicted geometry of the BPW91/cc-PVDZ calculations to help assess how much the observed Raman vibrational frequencies reflect the structure and bond order of the 2-fluorenylnitrenium ion. Selected optimized geometry structural parameters from the BPW91/cc-PVDZ calculations are shown in Table 2. Figure 3 presents selected schematic views of the optimized geometry for the 2-fluorenylnitrenium ion (the atoms are labeled with the numbering scheme used in Table 2 and the BPW91/cc-PVDZ computations).

Table 2. Selected Optimized Geometry Parameters from BPW91/cc-PVDZ Calculations for the Ground Singlet Electronic State of the 2-Fluorenylnitrenium Ion (see text)[a]

structural parameter	BPW91/cc-PVDZ calcd value	structural parameter	BPW91/cc-PVDZ calcd value
C12−N14	1.3077	C2−C1−C6	118.4
C11−C12	1.4732	C1−C2−C3	122.0
C10−C11	1.3701	C2−C3−C4	120.5
C7−C10	1.4373	C3−C4−C5	118.1
C12−C13	1.4696	C4−C5−C6	121.1
C8−C13	1.3685	C4−C5−C7	130.3
C8−C9	1.5122	C6−C5−C7	108.5
C4−C5	1.4230	C1−C6−C5	119.9
C3−C4	1.3907	C1−C6−C9	129.8
C2−C3	1.4202	C5−C6−C9	110.3
C6−C9	1.5081	C5−C7−C8	109.0
C1−C6	1.3947	C5−C7−C10	129.5
C1−C2	1.4082	C8−C7−C10	121.5
C5−C6	1.4400	C7−C8−C9	109.5
C5−C7	1.4294	C7−C8−C13	120.2
C7−C8	1.4497	C9−C8−C13	130.3
N14−H	1.0405	C6−C9−C8	102.7
C1−H	1.0975	C7−C10−C11	118.7
C2−H	1.0986	C10−C11−C12	121.2
C3−H	1.0972	C11−C12−C13	118.7
C4−H	1.0973	C11−C12−N14	124.8
C9−H19, C9−H20	1.1098	C13−C12−N14	116.5
C10−H	1.0972	C8−C13−C12	119.6
C11−H	1.0994	C12−N14−H24	110.6
C13−H	1.0982		

[a] The complete BPW91/cc-PVDZ computed optimized geometry parameters are available as Supporting Information. Bond lengths are in Å and bond angles are in deg. The atom numbers are those shown in Figure 3.

Examination of the bond length parameters in Table 2 shows that the C−N bond length is relatively short (1.3077 Å) and there is noticeable C−C bond length alternation in both phenyl rings. The 1.3077 Å C−N bond length is much closer to that for a typical C═N bond (1.28 Å) than a C−N bond (1.40 Å)[42] and this indicates the 2-fluorenylnitrenium ion has iminocyclohexadienyl character similar to that found for the 4-biphenylylnitrenium ion[28] and the four *N*-methyl-*N*-phenylnitrenium ions.[31] It is interesting that the 2-fluorenylnitrenium ion has a noticeably shorter C−N bond length (1.3077 Å) than that found from BPW91/cc-PVDZ computations for the four *N*-methyl-*N*-phenylnitrenium ions where the C−N bond lengths for the singlet states ranged from 1.317 to 1.323 Å.[31] The corresponding C−N bond length in the diphenylnitrenium ion was found to be ~1.351 Å, indicating a weaker imine/cyclohexadienyl character for this ion (since the charge delocalization is spread over two phenyl rings).[28,43]

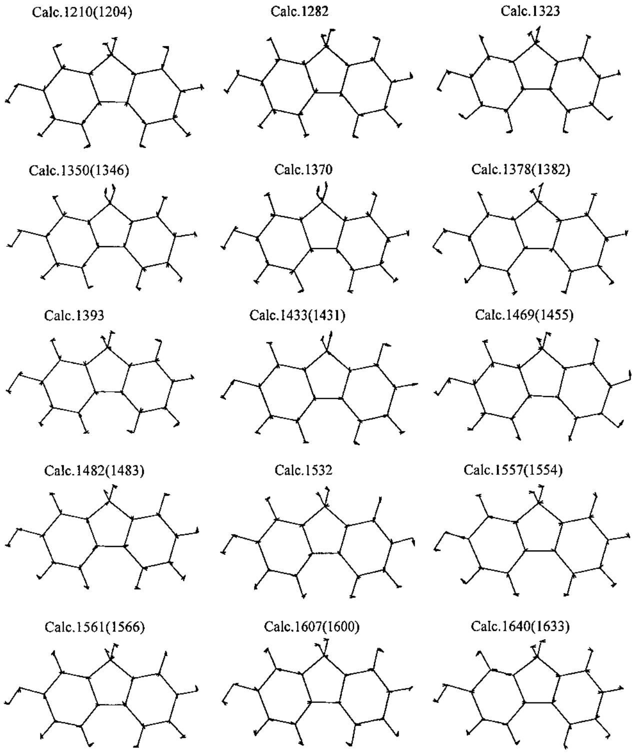

Figure 2. Diagrams are shown for fifteen vibrational modes of the 2-fluorenylnitrenium ion (ν_{11} to ν_{25}). Their normal mode vibrational motions are depicted in terms of internal coordinates by arrows as determined from the BPW91/cc-PVDZ computations. Each diagram is labeled with the DFT computed vibrational frequency (in cm^{-1}) and the Raman experimental value is shown in parentheses if applicable.

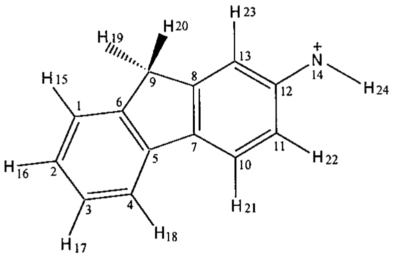

Figure 3. Diagram of the 2-fluorenylnitrenium ion with the atoms numbered 1−24. The numbering of the atoms is those shown in Tables 1 and 2 and in the Supporting Information for the BPW91/cc-PVDZ computations.

A symmetric aromatic C═C stretch vibrational mode in the 1568−1628 cm^{-1} region was found to be indicative of the degree of imine/quinoidal character of arylnitrenium ions.[28,31] The analogous modes in the 2-fluoronitrenium ion are ν_{11} (experiment at 1633 cm^{-1} and calculated at 1640 cm^{-1}) for the phenyl ring to which the nitrogen atom is attached and ν_{12} (experiment at ~1600 cm^{-1} and calculated at 1607 cm^{-1}) for the phenyl ring without the nitrogen atom attached. These values for the symmetric aromatic C═C stretch modes indicate that both phenyl rings have significant quinoidal character with the first phenyl ring (to which the nitrogen atom is attached) having substantially more quionoidal character than the other phenyl ring. This is consistent with the size of the differences found for the bond alternation in these two phenyl rings: the first ring has C12−C11 = 1.4732 Å, C11−C10 = 1.3701 Å, C10−C7 = 1.4373 Å and C12−C13 = 1.4696 Å, C13−C8 = 1.3685 Å, C8−C9 = 1.5122 Å compared to C4−C5 = 1.4230 Å, C4−C3 = 1.3907 Å, C3−C2 = 1.4202 Å and C9−C6 = 1.5081 Å, C6−C1 = 1.3947 Å, C1−C1 = 1.4082 Å for the second phenyl ring. Our results for the 2-fluorenylnitrenium ion exhibit stronger bond alternation in the first phenyl ring compared to the four *N*-methyl-*N*-phenylnitrenium ions recently investigated by Toscano, Cramer, and Falvey and co-workers[31] using BPW91/cc-PVDZ computations: r_3 = 1.427 Å, r_5 = 1.380 Å, and r_7 = 1.458 Å for the Me para-substituted derivative; r_3 = 1.424 Å, r_5 = 1.379 Å, and r_7 = 1.458 Å for the Cl para-substituted derivative; r_3 = 1.438 Å, r_5 = 1.374 Å, and r_7 = 1.457 Å for the Ph para-substituted derivative; r_3 = 1.434 Å, r_5 = 1.373 Å, and r_7 = 1.462 Å for the MeO para-substituted derivative.[31] This and the stronger C−N bond for the 2-fluorenylnitrenium ion indicates that it has a stronger iminocyclohexadienyl cation

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character for its first phenyl ring compared to the four *N*-methyl-*N*-phenylnitrenium ions[31] recently studied. This is consistent with the 2-fluorenylnitrenium ion ν_{11} symmetric C═C aromatic stretch mode frequency (experimental value of 1633 cm^{-1} and calculated value of 1640 cm^{-1}) being at higher frequency compared to the analogous modes in the four *N*-methyl-*N*-phenylnitrenium ions (which range from 1604 to 1628 cm^{-1} for the experiment and from 1604 to 1629 cm^{-1} for the calculations).[31] The second phenyl ring of the 2-fluorenylnitrenium ion also has significant cyclohexadienyl character with somewhat weaker bond alternation than in the four *N*-methyl-*N*-phenylnitrenium ions. This is consistent with the 2-fluorenylnitrenium ion ν_{12} aromatic C═C stretch mode vibrational frequency (~1600 cm^{-1} for the experiment and ~1607 cm^{-1} for the calculation).

It is interesting to compare the BPW91/cc-PVDZ computed structures and Raman band vibrational frequencies for the 2-fluorenylnitrenium ion to results reported for the *N*-(4-biphenylyl)-*N*-methylnitrenium ion.[31] Both of these ions contain two phenyl rings, and two symmetric C═C aromatic stretch vibrational modes associated with each of the phenyl rings are experimentally observed in either the transient resonance Raman spectrum (this work) or the TRIR spectrum.[31] However, these two modes for the 2-fluorenylnitrenium ion are at noticeably higher vibrational frequencies (~1633 and ~1600 cm^{-1} in the Raman experiment) compared to the *N*-(4-biphenylyl)-*N*-methylnitrenium ion (~1612 and ~1584 cm^{-1}, respectively, in the TRIR experiment).[31] This in combination with the shorter C−N bond length and more pronounced bond alternation in the first phenyl ring observed in the 2-fluorenylnitrenium ion indicates that it has a substantially stronger iminocyclohexadienyl cation character than the *N*-(4-biphenylyl)-*N*-methylnitrenium ion. This suggests that the bridging carbon bonds in the fluorene moiety of the 2-fluorenylnitrenium ion help promote further charge delocalization into the phenyl ring compared to the single carbon−carbon bridging of the two phenyl rings in the *N*-(4-biphenylyl)-*N*-methylnitrenium ion. The bridging carbon bonds in the fluorene appear to "tilt" in the same plane the two phenyl groups closer together (note the C6−C5−C7 and C5−C7−C8 bond angles are ~108° instead of ~120°), allowing better interaction or delocalization of the cation charge in the 2-fluoenylnitrenium ion. The 2-fluorenylnitrenium ion has a C5−C7 bond length of 1.4294 Å compared to a bond length of ~1.454 Å for the analogous (r1) bond in the *N*-(4-biphenylyl)-*N*-methylnitrenium ion,[31] and this is consistent with a greater interaction between the two phenyl rings in the 2-fluorenylnitrenium ion and its greater iminocyclohexadienyl character. This greater delocalization of the cation charge and greater iminocyclohexadienyl character of the 2-fluorenylnitrenium ion likely increases its stability and lifetime. This is consistent with the about 2 orders of magnitude longer lifetime observed in water solutions for the 2-fluorenylnitrenium ion compared to the 4-biphenylylnitrenium ion.[21]

Our demonstration of the utility of transient resonance Raman spectroscopy to directly examine arylnitrenium ions (like the 2-fluorenylnitrenium ion reported in this paper) nicely complements TRIR work and allows the structure and bonding of the arylnitrenium ions to be more fully investigated. Since Raman and IR spectroscopies arise from different molecular properties, their spectra often exhibit vibrational bands that are either not present or weak in intensity in the other form of vibrational spectroscopy. Thus, it is most desirable to obtain both Raman and IR spectra of the system of interest to best understand its structure and bonding via vibrational spectroscopy. Since arylnitrenium ions are of great interest in biological systems, it is also important to characterize the structure and bonding of these short-lived species in a largely aqueous environment (an environment similar to the biological system of interest). Raman spectroscopy can readily be applied to samples in water solvent. Our transient resonance Raman spectrum for the 2-fluorenylnitrenium ion is to our knowledge the first vibrational spectroscopic characterization of a short-lived arylnitrenium ion (i.e. generated photochemically) in a largely aqueous system (75% water/25% acetonitrile by volume). We are currently exploring the structure and bonding of a variety of arylnitrenium ions and their chemical reactions in largely aqueous systems using time-resolved resonance Raman spectroscopy and results from this work will be reported in due course.

Conclusions

We report the first vibrational spectrum for the 2-fluorenylnitrenium ion and the first transient resonance Raman spectroscopic characterization of a short-lived arylnitrenium ion. This study is also to our knowledge the first vibrational characterization of a short-lived arylnitrenium ion (i.e. generated photochemically) in a mainly water solvent system (75% water/25% acetonitrile by volume). The fundamental Raman band vibrational frequencies observed in the transient Raman spectrum displayed very good agreement with computed vibrational frequencies from BPW91/cc-PVDZ density functional theory calculations for the singlet ground state 2-fluorenylnitrenium ion. Our results verify the previous assignment of McClelland and co-workers[21] of the 460 nm transient absorption band observed after ultraviolet photolysis of 2-azidofluorene in water/acetonitrile or water solvents to the singlet 2-fluorenylnitrenium ion. Both our transient resonance Raman experiments and DFT computations indicate the singlet 2-fluorenylnitrenium ion has a large amount of iminocyclohexadienyl cation character with substantial charge delocalization over both phenyl rings of the fluorene structure. The 2-fluorenylnitrenium ion appears to have a stronger imine character and larger bond alternation in its first phenyl ring (to which the nitrogen atom is attached) compared to the four *N*-methyl-*N*-phenylnitrenium ions recently characterized by Toscano, Cramer, Falvey, and co-workers.[31]

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Supporting Information Available: Further details of the synthesis and characterization of the 2-azidofluorene precursor compound and selected output from the density functional theory computations for the singlet 2-fluorenylnitrenium ion (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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