Transient-Resonance Raman and Density Functional Theory Investigation of 4-Biphenylylnitrenium, 2-Fluorenylnitrenium, and Diphenylnitrenium Ions

Peizhi Zhu, Shing Yau Ong, Pik Ying Chan, Yuen Fan Poon, King Hung Leung, and David Lee Phillips*[a]

Abstract: We present transient-resonance Raman spectra for the 4-biphenylylnitrenium, diphenylnitrenium, and 2-fluorenylnitrenium ions. These spectra display a number of fundamental vibrational bands whose frequencies exhibit good agreement with those computed using BPW91/cc-PVDZ density functional theory calculations for the singlet ground states of the 4-biphenylylnitrenium, diphenylnitrenium, and 2-fluorenylnitrenium ions. Comparison of these arylnitrenium ions with each other and with previous results for structurally similar biphenyl radical cations indicates that the degree of iminocyclohexadienyl character observed in these arylnitrenium ions depends on the relative orientation of the two phenyl rings, the nature of the nitrenium ion moiety, and the ability of the biphenyl-like group to accommodate positive charge through formation of a more planar-like structure with quinoidal-like character.

Keywords: arylnitrenium ions · cations · density functional calculations · Raman spectroscopy

Introduction

Arylnitrenium ions are thought to have a key role in chemical carcinogenesis, and there is much interest in their chemical reactions and properties.[1–18] Aromatic amines like 2-acetylaminofluorene may be enzymatically converted into sulfate esters of the analogous *N*-hydroxylamines, and in aqueous environments a sulfate anion will spontaneously leave these esters to produce an arylnitrenium ion.[13, 17] These arylnitrenium ions can in some cases (such as the 2-fluorenylnitrenium ion) be selectively trapped by guanine bases in DNA, and this is thought to result in carcinogenic mutations.[8–10, 14, 18] Arylnitrenium ions are usually very short-lived and problematic to investigate in room-temperature solutions. Photochemical methods have been recently developed by several groups to produce arylnitrenium ions.[19–32] This has allowed a range of laser spectroscopy techniques to be applied to study arylnitrenium ions in room-temperature solutions.[19–33] Transient-absorption experiments have been used to investigate several arylnitrenium ions to determine their lifetimes and rate constants for reactions with other compounds.[19–28, 30, 31] Toscano and Falvey and co-workers[29] examined the diphenylnitrenium ion solution in acetonitrile using time-resolved infrared methods (TRIR). This study demonstrated that the diphenylnitrenium ion has an iminocyclohexadienyl cation-like character.[29] These TRIR experiments were extended to a series of four *N*-methyl-*N*-phenylnitrenium ions in solution in acetonitrile, and substituent effects on the symmetrical aromatic C=C stretch mode(s) in the 1580 to 1628 cm^{-1} region were investigated.[32] This work found excellent agreement between BPW91/cc-PVDZ density functional theory computed vibrational frequencies and the experimentally observed infrared vibrational frequencies.[32] Their BPW91/cc-PVDZ computational results displayed significant bond alternation in the phenyl rings with shorter C–N bond lengths and noticeable positive charge delocalization into the phenyl rings.[32] We recently reported the first transient-resonance Raman spectra and the first time-resolved vibrational spectrum taken in a largely aqueous solvent for an arylnitrenium ion (the 2-fluorenylnitrenium ion).[33] The transient-resonance Raman spectrum displayed ten fundamental vibrational bands in the 1100–1700 cm^{-1} fingerprint region and several combination bands in the 2400–3300 cm^{-1} region. The transient-resonance Raman spectra vibrational frequencies exhibited very good agreement with those calculated from BPW91/cc-PVDZ computations. Our results demonstrated that the 2-fluorenylnitrenium ion had a noticeably larger degree of iminocyclohexadienyl character with a large amount of positive charge delocalization into both phenyl rings than previously for nitrenium ions examined with time-resolved vibrational spectroscopy methods.[29, 32, 33] However, it is still not clear what governs the degree of iminocyclohexadienyl character and extent of charge delocalization of

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[a] Prof. Dr. D. L. Phillips, P. Zhu, S. Y. Ong, P. Y. Chan, Y. F. Poon, Dr. K. H. Leung
Department of Chemistry, University of Hong Kong
Pokfulam Road (Hong Kong)
Fax: (+852)2857-1586
E-mail: phillips@hkucc.hku.hk

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arylnitrenium ions containing two phenyl rings with the second ring attached at a *para*-position relative to the nitrenium ion moiety.

In this paper, we report the first transient-resonance Raman spectra for the singlet 4-biphenylylnitrenium and diphenylnitrenium ions. We also report a higher signal to noise transient-resonance Raman spectrum of the 2-fluorenylnitrenium ion that displays a number of new fundamental vibrational frequencies. These spectra were obtained under similar conditions in a largely aqueous solvent system. We have done BPW91/cc-PVDZ computations to find the optimized geometry and computed vibrational frequencies for the singlet 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions. The computed vibrational frequencies show good agreement with the experimental Raman bands observed for the 2-fluorenylnitrenium, the 4-biphenylylnitrenium, and diphenylnitrenium ions and with the infrared bands previously reported for the diphenylnitrenium ion.[29] Our results demonstrate the degree of iminocyclohexadienyl character and the amount of positive charge delocalization into the phenyl rings depend on the relative orientation of the phenyl rings with respect to each other and on the character of the nitrenium ion moiety. We compare our results with those of other cations with similar structures and briefly discuss how the iminocyclohexadienyl character of arylnitrenium ions with two phenyl rings may be affected by substituent effects.

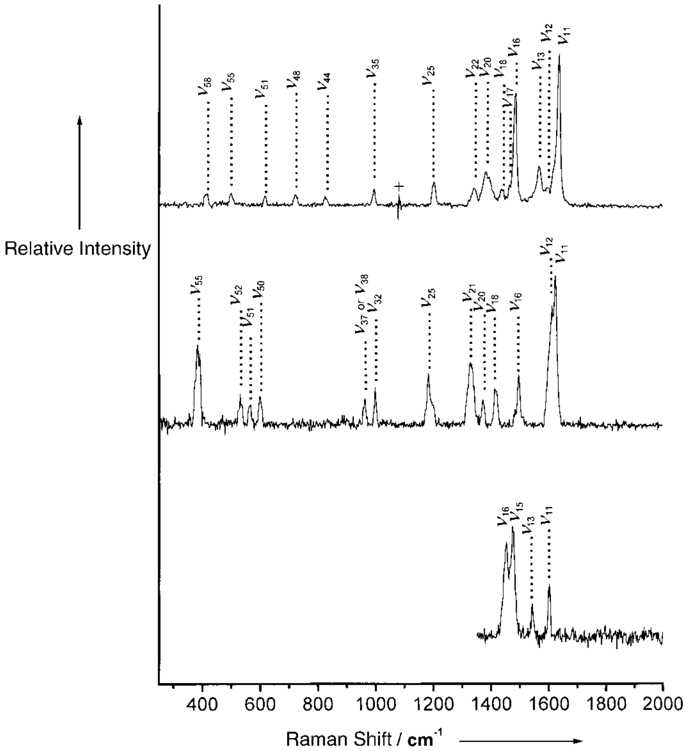


Figure 1. Transient-resonance Raman spectra of the 2-fluorenylnitrenium ion (top), the 4-biphenylylnitrenium ion (middle), and diphenylnitrenium ion (bottom) obtained in a largely aqueous solution (60% water/40% acetonitrile by volume) with 266 nm pump and 416 nm probe wavelengths. The tentative assignments of the larger Raman bands are shown above the spectra (see text and Table 1 for more details). The transient-resonance Raman spectra were found by subtracting a probe-only spectrum and a pump-only spectrum from a pump–probe spectrum to remove solvent and precursor bands. Use of a different precursor than the 2-fluorenylnitrenium and 4-biphenylylnitrenium ions for generating the diphenylnitrenium ion resulted in a large Rayleigh background and interfering bands in the lower frequency region so only the 1350–2000 cm^{-1} region is shown for this spectrum. The dagger marks solvent subtraction artifacts, stray light, or ambient light artifacts.

Results and Discussion

Laser flash photolysis of 4-azidobiphenyl or 2-azidofluorene solutions in water/acetonitrile has been shown to give intense transient absorption bands on the nanosecond to microsecond timescale with a maximum at ≈460 nm that were assigned to the 4-biphenylylnitrenium ion and 2-fluorenylnitrenium ion, respectively.[18, 21] Similarly, photolysis of *N*-(diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate has been shown to give rise to the formation of the diphenylnitrenium ion with transient absorption bands at ≈425 to 430 nm and ≈650 to 670 nm.[27, 29] The 2-fluorenylnitrenium ion was observed to have an appearance lifetime of about 100 ps.[25] These nitrenium ions appear to be formed very quickly so that a 10 ns delay between the pump and probe pulses should provide sufficient time to allow significant formation of the nitrenium ions to examine. The probe wavelength (416 nm) used in the transient-resonance Raman experiments is within the transient absorption bands (on the blue part). Thus we expect our transient-resonance Raman spectra to probe the identity and structure of the species responsible for these broad characteristic transient absorption bands that were assigned to arylnitrenium ions. Figure 1 displays the 416 nm transient-resonance Raman spectra of the 2-fluorenylnitrenium (top), 4-biphenylylnitrenium (middle), and diphenylnitrenium (bottom) ions with the larger Raman bands labeled with their preliminary vibrational assignments.

Table 1 lists the vibrational frequencies and preliminary assignments for the transient-resonance Raman bands observed for the spectra of the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions shown in Figure 1. Several previous studies used time-resolved vibrational spectra (either infrared or Raman) and comparison with density functional theory calculated vibrational frequencies to assign several nitrenium ions (including the diphenylnitrenium and 2-fluorenylnitrenium ions) to their singlet ground electronic states,[29, 32, 33] and we expect that the 4-biphenylylnitrenium ion is also likely in its singlet ground electronic state. Recent TRIR and TR^3 (time-resolved resonance Raman) studies found excellent agreement between the experimental vibrational frequencies and those values computed from BPW91/ccPVDZ computations for five nitrenium ions.[32, 33] We have done similar calculations for the singlet ground electronic state of the 4-biphenylylnitrenium and diphenylnitrenium ions (calculations for the 2-fluorenylnitrenium ion were previously reported in reference [33]) to find the optimized geometry and calculated vibrational frequencies. Inspection of Table 1 shows that the experimental frequencies for the transient-resonance Raman bands generally display good agreement with the BPW91/cc-PVDZ calculated values and can serve as a reasonable tool for identification of the photoproduct species. Our results indi-

Table 1. Experimental Raman vibrational frequencies observed in the transient-resonance Raman spectrum in Figure 1 for the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions. Tentative vibrational band assignments are also shown based on comparison with computed vibrational frequencies from BPW91/cc-PVDZ calculations for the ground singlet electronic state of the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions (see text).

A. 2-fluorenylnitrenium ion

vibrational mode	BPW91/ cc-PVDZ calcd [in cm^{-1}]	transient-resonance Raman frequency shift [in cm^{-1}][a]
ν_{60}, inter-ring def. (in plane)	354	
ν_{58}, central ring def. (in plane)	**403**	**407**
ν_{57}, ring def. (out of plane)	438	
ν_{56}, ring def. (out of plane)	453	
ν_{55}, ring def. (in plane)	**499**	**500**
ν_{54}, ring def. (in plane)	529	
ν_{52}, ring def. (out of plane)	564	
ν_{51}, CCC bend	**621**	**616**
ν_{50}, CCC bend + CH$_2$ twist	686	
ν_{49}, CCC bend	713	
ν_{48}, CCC bend	**729**	**721**
ν_{47}, C−H bend and N−H bend (out of plane)	738	
ν_{45}, C−H bend and N−H bend (out of plane)	805	
ν_{44}, C−H bend and N−H bend (out of plane)	**816**	**824**
ν_{43}, CH bend (out of plane) + CH$_2$ rock	853	
ν_{36}, C−C stretch	982	
ν_{35}, C−H bend	**1000**	**994**
ν_{34}, C−H bend	1013	
ν_{33}, C−H & N−H bend (in the plane)	1093	
ν_{32}, C−H & N−H bend (in the plane)	1109	
ν_{31}, C−H & N−H bend (in the plane)	1114	
ν_{30}, CH$_2$ twist	1123	
ν_{29}, CH$_2$ wag + C−H & N−H bending (in the plane)	1141	
ν_{28}, C−H bend	1155	
ν_{27}, CH$_2$ wag + C−H & N−H bend (in the plane)	1174	
ν_{26}, CH$_2$ wag + C−H & N−H bend (in the plane)	1187	
ν_{25}, C−CH$_2$ stretch + C−H + N−H bend (in the plane)	**1210**	**1201 (1204)[b]**
ν_{24}, C−CH$_2$ stretch + C−H & N−H bend (in the plane)	1282	
ν_{23}, C−CH$_2$ stretch + C−H & N−H bend (in the plane)	1323	
ν_{22}, CH$_2$ scissor + C−H & N−H bend (in the plane)	**1350**	**1342 (1346)[b]**
ν_{21}, CH$_2$ scissor + C−H & N−H bend (in the plane)	1370	
ν_{20}, N−H & C−N bending (in the plane)	**1378**	**1383 (1382)[b]**
ν_{19}, CH$_2$ wag + C−H & N−H bend (in the plane)	1393	
ν_{18}, CH$_2$ scissor + C−H & N−H bend (in the plane)	**1433**	**1435 (1431)[b]**
ν_{17}, C−H bend	**1469**	**1460 (1455)[b]**
ν_{16}, C−C stretch	**1482**	**1486 (1483)[b]**
ν_{15}, C−C stretch	1532	
ν_{14}, C−C stretch	**1557**	**(1554)[b]**
ν_{13}, C−C stretch	**1561**	**1567 (1566)[b]**
ν_{12}, ring 3 C−C stretch	**1607**	**1600 (1600)[b]**
ν_{11}, ring 1 C−C stretch	**1640**	**1637 (1633)[b]**

B. 4-biphenylylnitrenium ion

vibrational mode	BPW91/ cc-PVDZ calcd [in cm^{-1}]	transient-resonance Raman frequency shift [in cm^{-1}][a]
ν_{56}, ring def.	360	
ν_{55}, ring def.	**377**	**386**
ν_{54}, C−H bend	416	
ν_{53}, ring def.	457	
ν_{52}, C−H bend (out of plane)	**529**	**530**
ν_{51}, C−H bend (in plane)	**550**	**563**
ν_{50}, ring def. (in plane)	**587**	**589**
ν_{49}, ring def. (in plane)	607	
ν_{39}, CH bend (out of plane)	940	
ν_{38}, C−H bend (in plane)	**951**	**962?**
ν_{37}, C−H bend (out of plane)	**972**	**962?**
ν_{36}, C−H bend (out of plane)	975	
ν_{35}, C−H bend (in the plane)	980	
ν_{34}, N−H & C−N bend (out of plane)	982	
ν_{33}, CH bend + NH bend (out of plane)	990	
ν_{32}, C−H bend	**1003**	**998**

cate that the singlet 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions are associated with the intense transient absorption bands observed after photolysis of 2-azidofluorene ($\approx$460 nm), 4-azidobiphenyl ($\approx$460 nm), and *N*-(diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate ($\approx$425 to 430 nm), respectively. This is in good agreement with assignments previously put forward by several groups.[18, 21, 27]

The resonance Raman spectra in Figure 1 usually have intense bands associated with the C=C stretches of the phenyl rings (particularly the ring to which the N−H group is attached) and the C−N−H group. Figures 2–4 display simple schematic diagrams of the normal mode descriptions for the vibrational modes observed in the transient-resonance Raman spectra for the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions, respectively. Examination of Figure 2 as well as Figures 3 and 4 shows that the normal mode descriptions are reasonably complex with contributions from a number of internal coordinates. We note the computed vibrational frequencies agree well with the values observed in the experimental Raman spectra (see Table 1). This suggests that it would be worthwhile to use the optimized geometry from the BPW91/cc-PVDZ calculations to aid in determining how much the observed Raman vibrational frequencies reflect the structure and bond order of the three nitrenium ions investigated here. Selected optimized geometry structural parameters from the BPW91/cc-PVDZ calculations are given in Table 2. Scheme 1 presents simple schematic diagrams for the 2-fluorenylnitrenium (top), 4-biphenylylnitrenium (middle), and diphenylnitrenium (bottom) ions with their atoms numbered as listed in Table 2.

Examination of Table 2 shows that the C−N bond length parameters are relatively short (1.3077 Å for 2-fluorenylnitrenium, 1.3083 Å for 4-biphenylylnitrenium, and 1.3512 Å for diphenylnitrenium ions, respectively), and this indicates they have some imine character. The C−N bond lengths for 2-fluorenylnitrenium and 4-biphenylylnitrenium ions are close to those for a typical C=N bond (1.28 Å) and somewhat stronger than

Table 1. (Continued).

B. 4-biphenylylnitrenium ion		
vibrational mode	BPW91/ cc-PVDZ calcd [in cm^{-1}]	transient-resonance Raman frequency shift [in cm^{-1}][a]
ν_{31}, C–C stretch	1021	
ν_{27}, C–H bend (in plane)	1155	
ν_{26}, C–H bend (in the plane)	1165	
ν_{25}, C–H bend (in the plane)	**1188**	**1184**
ν_{24}, CCC asym. bend	1264	
ν_{23}, C–CH$_2$ stretch + C–H & N–H bend (in the plane)	1289	
ν_{22}, CCC sym. bend (in the plane)	1315	
ν_{21}, C–H & N–H bend (in the plane)	**1353**	**1334**
ν_{20}, N–H & C–H bending (in the plane)	**1387**	**1373**
ν_{19}, CH bend	1402	
ν_{18}, C–H & N–H bend (in the plane)	**1429**	**1422**
ν_{17}, CCC bend (in plane)	1451	
ν_{16}, C–C stretch	**1476**	**1496**
ν_{15}, C–C stretch	1525	
ν_{13}, C–C stretch	1554	
ν_{12}, ring 2 C–C stretch	**1602**	**1607**
ν_{11}, ring 1 C–C stretch	**1625**	**1625**
C. diphenylnitrenium ion		
vibrational mode	BPW91/ cc-PVDZ calcd [in cm^{-1}]	time-resolved IR or Raman frequency [in cm^{-1}][c]
ν_{20}, CCC sym. stretch	1373	
ν_{19}, C–C and C–N stretch	**1401**	**1392 (IR)**
ν_{18}, C–C sym. str.	**1441**	**1442 (IR)?**
ν_{17}, C–C sym. str.	**1441**	**1442 (IR)?**
ν_{16}, C–C sym. str.	**1451**	**1455 (Raman)**
ν_{15}, C–N–C asym. str. and CH in plane bend	**1467**	**1478 (Raman)**
ν_{14}, C–C stretch	1524	
ν_{13}, C–C stretch	**1525**	**1543 (Raman)**
ν_{12}, C–C stretch	**1586**	**1568 (IR)[c]**
ν_{11}, C–C stretch	**1604**	**1604 (Raman)**

[a] Estimated uncertainty in Raman shift is ±3 cm^{-1}. [b] Values in parentheses are Raman shifts observed in the preliminary transient-resonance Raman spectrum reported in reference [33]. [c] IR frequencies are those reported in reference [29].

those previously found for four *para*-substituted *N*-methyl-*N*-phenylnitrenium ions (ranging from 1.317 to 1.323 Å).[32] The value for the diphenylnitrenium ion is about half way between a typical C=N bond (1.28 Å) and a typical C–N bond (1.40 Å) which indicates it has a substantially weaker iminocyclohexadienyl character due to the diphenylnitrenium ion having two resonance forms (one with a C–N bond and one with a C=N bond).

A symmetric aromatic C=C stretch vibrational mode in the 1568 to 1628 cm^{-1} region was previously found to be an indicator for the amount of imine/cyclohexadienyl character for several arylnitrenium ions.[29, 32] The corresponding modes are ν_{11} (experiment at 1637, 1625, and 1604 cm^{-1} and calculated at 1640, 1625, and 1604 cm^{-1} for the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions, respectively) for the phenyl ring to which the nitrogen atom is attached and ν_{12} (experiment at 1600 and 1607 cm^{-1} and calculated at 1607 and 1602 cm^{-1} for the 2-fluorenylnitrenium and 4-biphenylylnitrenium ions, respectively) for the phenyl ring without the nitrogen atom attached. These values for the symmetric aromatic C=C stretch suggest that both phenyl rings in these ions have noticeable cyclohexadienyl character. The phenyl ring to which the nitrogen atom is attached has greater cyclohexadienyl character than the phenyl ring without the nitrogen atom attached in the case of the 2-fluorenylnitrenium and 4-biphenylylnitrenium ions. This is in agreement with the degree of differences between the bond alternation pattern in the two types of phenyl rings (e.g. with and without the nitrogen atom attached) of the 2-fluorenylnitrenium and 4-biphenylylnitrenium ions: the first ring has C12–C11 of 1.4732 Å; C11–C10 of 1.3701 Å; C10–C7 of 1.4373 Å and C12–C13 of 1.4696 Å; C13–C8 of 1.3685 Å; C8–C9 of 1.5122 Å compared with C4–C5 of 1.4230 Å; C4–C3 of 1.3907 Å; C3–C2 of 1.4202 Å and C9–C6 of 1.5081 Å; C6–C1 of 1.3947 Å; C1–C1 of 1.4082 Å for the second phenyl ring for the 2-fluorenylnitrenium ion and the first ring has C10–C11 of 1.4652 Å; C11–C12 of 1.3693 Å; C12–C7 of 1.4492 Å and C10–C9 of 1.4644 Å; C9–C8 of 1.3707 Å; C8–C7 of 1.4441 Å compared with C5–C6 of 1.4334 Å; C6–C1 of 1.3919 Å; C1–C2 of 1.4104 Å and C5–C4 of 1.4334 Å; C4–C3 of 1.3917 Å; C3–C2 of 1.4106 Å for the second phenyl ring for the 4-biphenylylnitrenium ion. The bond alternation is stronger in the first ring for the 2-fluorenylnitrenium ion than in the 4-biphenylylnitrenium ion and the four *para*-substituted *N*-methyl-*N*-phenylnitrenium ions studied by Toscano, Cramer, and Falvey and coworkers.[32]

It is interesting to make a comparison of the 2-fluorenylnitrenium ion structure and vibrational frequencies for the ν_{11} and ν_{12} symmetric aromatic C=C stretch vibrational modes for the two phenyl rings with those for the 4-biphenylylnitrenium and *N*-(4-biphenylyl)-*N*-methylnitrenium ions. The experimental vibrational frequencies for the ν_{11} and ν_{12} modes are 1637 and 1600 cm^{-1} for the 2-fluorenylnitrenium ion, 1625 and 1607 cm^{-1} for the 4-biphenylylnitrenium ion, and 1612 and 1584 cm^{-1} for the *N*-methyl-*N*-phenylnitrenium ion. These trends in the frequencies for the ν_{11} mode correlate very well with the C–N bond lengths and degree of imine character (e.g. 1.3077 Å for the 2-fluorenyl nitrenium ion, 1.3083 Å for the 4-biphenylylnitrenium ion, and 1.321 Å for the *N*-(4-biphenylyl)-*N*-methylnitrenium ion[32]) as well as the degree of cyclohexadienyl character of the phenyl ring to which the nitrogen atom is attached. The large degree of iminocyclohexadienyl character of the first phenyl ring in the 2-fluorenylnitrenium ion appears to be mainly due to its fluorene moiety, which induces an in-plane tilt of the two phenyl rings in its structure (note that the C6–C5–C7 and C5–C7–C8 bond angles are about 108° for the 2-fluorenylnitrenium ion compared with about 120° for the 4-biphenylylnitrenium and *N*-(4-biphenylyl)-*N*-methylnitrenium ions). This enables better interaction and hence delocalization of the cation

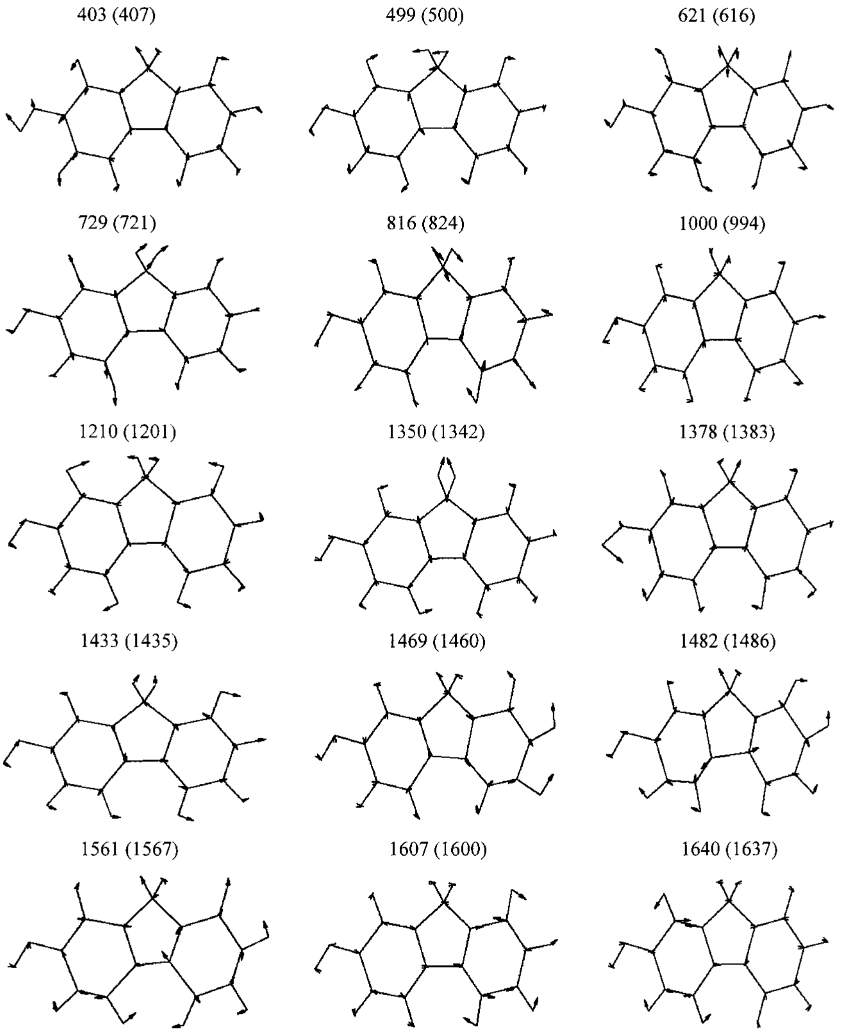


Figure 2. Diagrams are displayed for the fifteen vibrational modes of the 2-fluorenylnitrenium ion tentatively assigned to bands observed in the transient-resonance Raman spectrum shown in Figure 1. Their normal mode vibrational motions (enlarged by a factor of 2) are shown in terms of internal coordinates by arrows as deduced from the BPW91/cc-PVDZ calculations. Each diagram is marked with the DFT calculated vibrational frequency (in cm^{-1}), and the Raman experimental value is given in parentheses (see Table 1).

charge of the nitrenium ion group into the phenyl ring to which it is attached. The trend in the C–N bond lengths for these three nitrenium ions also correlates well with the degree of carbon double bond character of the C5–C7 bond connecting the two phenyl rings (1.4294 Å for the 2-fluorenylnitrenium ion, 1.4494 Å for the 4-biphenylylnitrenium ion, and 1.454 Å for the *N*-(4-biphenylyl)-*N*-methylnitrenium ion[32]). This is consistent with the amount of iminocyclohexadienyl character of the first phenyl ring (attached to the nitrenium ion group) and the vibrational frequencies of the ν_{11} symmetric aromatic C=C stretch vibrational modes.

The 4-biphenylylnitrenium ion and the *N*-(4-biphenylyl)-*N*-methylnitrenium ion only differ in the hydrogen atom attached to the nitrogen atom of nitrenium that is replaced by a methyl group. This substitution noticeably affects the structure and charge delocalization of the 4-biphenylylnitrenium ion moiety. The C–N bond and the C5–C7 bond (connecting the two phenyl rings) are somewhat shorter in the 4-biphenylylnitrenium ion (1.3083 and 1.4494 Å, respectively) than in the *N*-(4-biphenylyl)-*N*-methylnitrenium ion (1.321 and 1.454 Å, respectively[32]). This correlates with the larger degree of C–C bond alternation observed in both phenyl rings and the higher ν_{11} and ν_{12} symmetric aromatic C=C stretch experimental vibrational frequencies for the 4-biphenylylnitrenium ion (1625 cm^{-1} for ν_{11} and 1607 cm^{-1} for ν_{12}) compared with the *N*-(4-biphenylyl)-*N*-methylnitrenium ion (1612 and 1584 cm^{-1} from reference [32]). This indicates that the 4-biphenylylnitrenium ion has noticeably more iminocyclohexadienyl character than the *N*-(4-biphenylyl)-*N*-methylnitrenium ion. To better understand this behavior, it is useful to make comparisons with the biphenyl radical cation and some substituted radical cations.[34–46]

Oxidation of neutral biphenyl and substituted biphenyl compounds to form their corresponding radical cations in room-temperature solutions typically results in a more planar structure with some quinoidal-like character, although the structure remains nonplanar. For example, the S_0 state of biphenyl goes from an inter-ring twist angle of about 38°, an inter-ring C–C bond length of about 1.486 Å, and little C–C bond alternation in the phenyl rings to an inter-ring twist angle of about 19°, an inter-ring C–C bond length of about 1.444 Å, and appreciable C–C bond alternation in both phenyl rings ($\approx$1.433 Å to 1.379 Å to 1.403 Å) in the S_0 radical cation of biphenyl.[37–42, 45] The quinoidal character and charge delocalization is similar in both phenyl rings of the biphenyl radical cation and halo or methyl-substituted radical cations.[37–46] However, the nitrenium ion significantly interacts with the biphenyl moiety, and the charge delocalization is substantially different for the two phenyl rings in the arylnitrenium ions in which the C–C bond alternation is much stronger in the phenyl ring to which the nitrogen atom is attached, and this also influences the degree of imine character of the C–N bond. Our results for the 4-biphenylylnitrenium ion and comparison with previous results reported for the *N*-(4-biphenylyl)-*N*-methylnitrenium ion indicate that the $-NH^+$ group leads to greater interaction and a higher degree of iminocyclohexadienyl character than the $-NCH_3^+$ group. The larger stability and better charge delocalization of arylnitrenium ions having *para*-phenyl ring substitution on a phenylnitrenium ion (such as 2-fluorenylni-

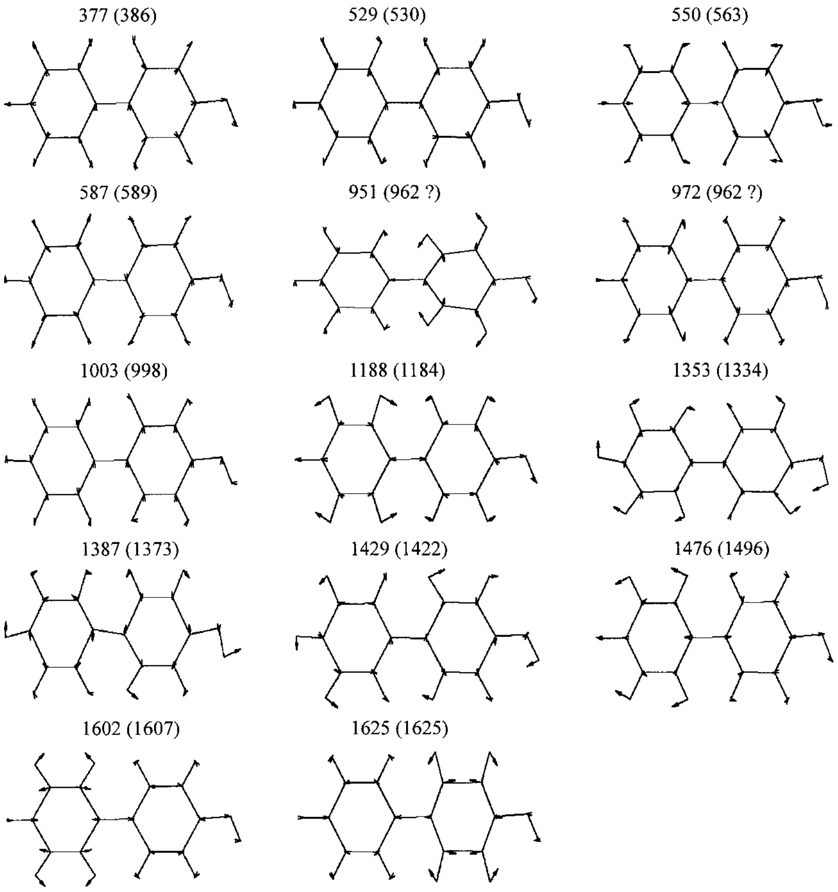


Figure 3. Diagrams are displayed for the fourteen vibrational modes of the 4-biphenylylnitrenium ion tentatively assigned to bands observed in the transient-resonance Raman spectrum shown in Figure 1. Their normal mode vibrational motions (enlarged by a factor of 2) are shown in terms of internal coordinates by arrows as deduced from the BPW91/cc-PVDZ calculations. Each diagram is marked with the DFT calculated vibrational frequency (in cm^{-1}), and the Raman experimental value is given in parentheses (see Table 1).

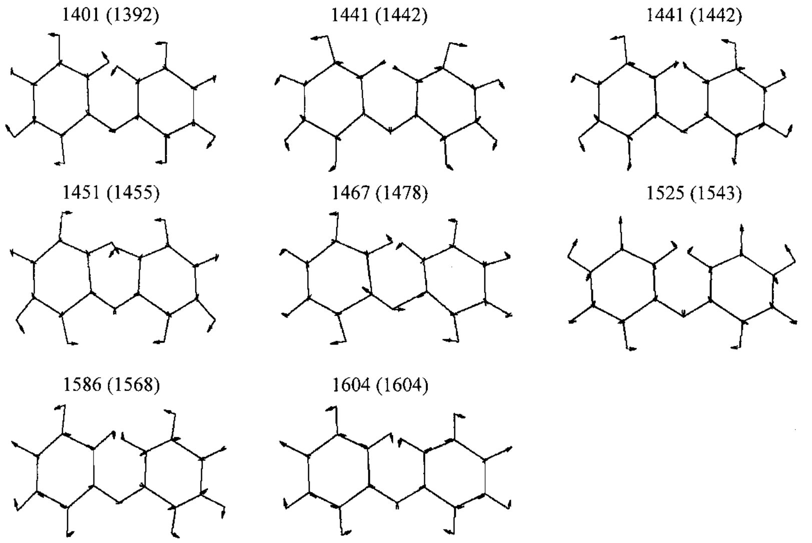


Figure 4. Diagrams are displayed for the eight vibrational modes of the diphenylnitrenium ion tentatively assigned to bands observed either in the transient-resonance Raman spectrum (shown in Figure 1) or the infrared spectrum reported in reference [29]. Their normal mode vibrational motions (enlarged by a factor of 2) are shown in terms of internal coordinates by arrows as deduced from the BPW91/cc-PVDZ calculations. Each diagram is marked with the DFT calculated vibrational frequency (in cm^{-1}), and the Raman experimental value is given in parentheses (see Table 1).

trenium, 4-biphenylylnitrenium, and *N*-(4-biphenylyl)-*N*-methylnitrenium ions) appear to be due to the ability of the biphenyl-like group to accommodate and delocalize the positive charge in both phenyl rings.

ortho-Substitution relative to the inter-ring C–C bond in halo- and methyl-substituted biphenyl radical cations results in less planarity and less quinoidal character.[43, 44, 46] This suggests that similar substitution in 4-biphenylylnitrenium type ions (like the 4-biphenylylnitrenium and *N*-(4-biphenylyl)-*N*-methylnitrenium ions examined here) could also cause noticeable weakening of the iminocyclohexadienyl character of the arylnitrenium ion. *ortho*-Substitution relative to the nitrenium ion attached to the phenyl ring will also likely exert noticeable influence on the degree of charge delocalization and iminocyclohexadienyl character of the arylnitrenium ion. Recent studies reported for *ortho*-fluorine substituents on singlet phenylnitrenes found that a single fluorine substitutent has a small bystander effect on remote cyclization that is not steric in origin, and two *ortho*-fluorine substituents have a substantial effect on the cyclization reaction.[47] At this time it is not clear to what degree *ortho*-substitution relative to the nitrenium moiety attached to a *para*-substituted phenyl ring will change its iminocyclohexadienyl character, and further work is needed to elucidate this behavior.

The diphenylnitrenium ion has the longest C–N bond length and lowest degree of iminocyclohexadienyl character of the *para*-substituted arylnitrenium ions so far examined by transient vibrational spectroscopy in room-temperature solutions. The charge delocalization is about the same in

Table 2. Selected optimized geometry parameters from BPW91/cc-PVDZ calculations for the ground singlet electronic state of the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions (see text). Bond lengths are in Å, and bond angles are in degrees. The atom numbers are those shown in Scheme 1.

A. 2-fluorenylnitrenium ion

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	**D(C6–C5–C7–C8)**	**180.0**

B. 4-biphenylylnitrenium ion

structural parameter	BPW91/ cc-PVDZ calcd value	structural parameter	BPW91/ cc-PVDZ calcd value
C1–C2	1.4104	C6–C1–C2	120
C2–C3	1.4106	C1–C2–C3	120.3
C3–C4	1.3917	C2–C3–C4	120
C4–C5	1.4334	C3–C4–C5	120.8
C5–C6	1.4334	C4–C5–C6	117.9
C6–C1	1.3919	C5–C6–C1	120.8
C5–C7	1.4494	C4–C5–C7	121
C7–C8	1.4441	C5–C7–C8	121.1
C8–C9	1.3707	C12–C7–C8	118.1
C9–C10	1.4644	C7–C8–C9	121.2
C10–C11	1.4652	C8–C9–C10	121.1
C11–C12	1.3693	C9–C10–C11	117.2
C12–C7	1.4492	C10–C11–C12	120.8
C10–N13	1.3083	C11–C12–C7	121.5
C1–H14, C3–H16	1.0972	C9–C10–N13	117
C2–H15	1.0984	C11–C10–N13	125.7
C8–H19	1.0954	C10–N13–H23	110.5
C4–H17, C6–H18	1.0959	**D(C6–C5–C7–C12)**	**−17.6**
C9–H20	1.0979		
C11–H21	1.0994		
C12–H22	1.0956		
N13–H23	1.0408		

C. diphenylnitrenium ion

structural parameter	BPW91/ cc-PVDZ calcd value	structural parameter	BPW91/ cc-PVDZ calcd value
C1–C2	1.4134	C6–C1–C2	119.6
C2–C3	1.4165	C1–C2–C3	121.2
C3–C4	1.3882	C2–C3–C4	120.2
C4–C5	1.4444	C3–C4–C5	119.6
C5–C6	1.4426	C4–C5–C6	119.0
C6–C1	1.3986	C5–C6–C1	120.2
C5–N7	1.3512	C4–C5–N7	125.9

both phenyl rings, and the structure has a higher degree of symmetry than the 2-fluorenylnitrenium and 4-biphenylylnitrenium ions. This appears to correlate with a greater intensity in the vibrational modes associated with the C–N bonds compared with the C–C bonds of the phenyl ring for the diphenylnitrenium ion and an apparent higher degree of mutual exclusive character between the infrared and Raman bands observed experimentally in the 1300 to 1700 cm^{-1} region. This illustrates the benefit of obtaining (where possible) both infrared and Raman spectra for species with higher symmetry. This enables one to observe more vibrational bands and better characterize the structure and bonding of the species of interest. Further experimental work to obtain vibrational bands over a wider range of frequencies for both the infrared and Raman spectra of the diphenylnitrenium ion should prove interesting and possibly be useful in testing various levels of theoretical methods and basis sets to calculate the optimized geometry and vibrational frequencies of arylnitrenium ions.

Conclusion

We report transient-resonance Raman spectra for the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions in room-temperature solutions. These spectra display a number of fundamental vibrational bands, and their frequencies exhibit reasonable agreement with those computed using BPW91/cc-PVDZ density functional theory calculations for the singlet ground state of the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions. These arylnitrenium ions display varying degrees of iminocyclohexadienyl character that depend on the relative orientation of the two phenyl rings and the nature of the nitrenium moiety (for example, a $-NH^+$ group leads to noticeably more iminocyclohexadienyl character than a $-NCH_3^+$ group when attached to the phenyl rings). Comparison of the 4-biphenylylnitrenium ion and related arylnitrenium ions to structurally similar biphenyl radical cations indicates that the nitrenium ion moiety can delocalize its charge into the *para*-substituted phenyl rings through the tendency of the biphenyl-like group to form a more planar radical cation. This ability appears to lead to the greater stability and lifetimes observed for these types of arylnitrenium ions and likely influences their chemical reactivity (this will be explored in more detail and results reported in due course).

Experimental Section

Synthesis of 2-azidofluorene, 4-azidobiphenyl, and *N*-(diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate precursors

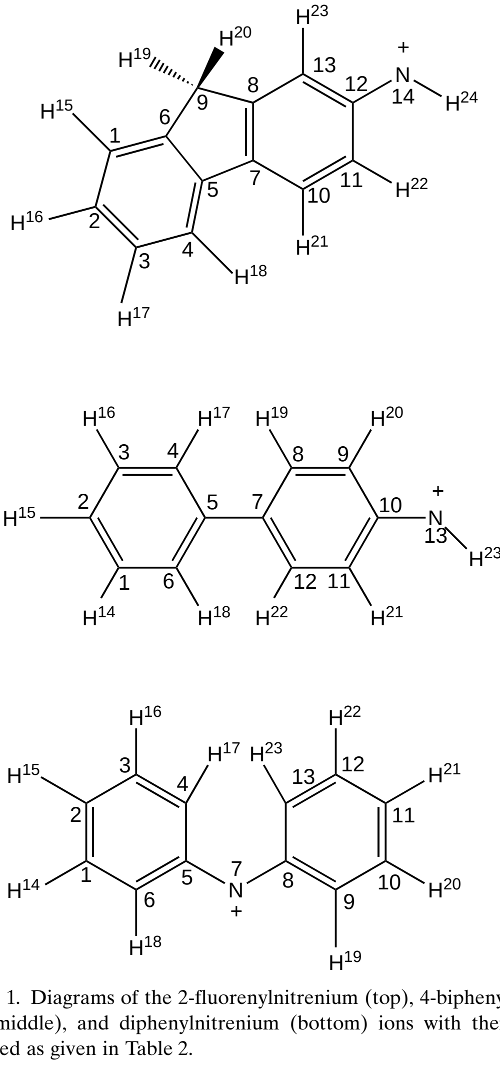
2-Azidofluorene: The compound 2-azidofluorene was synthesized based on previously reported procedures for the synthesis of azido

Table 2. (Continued).

C. diphenylnitrenium ion

structural parameter	BPW91/ cc-PVDZ calcd value	structural parameter	BPW91/ cc-PVDZ calcd value
N7–C8	1.3512	C5–N7–C8	125.2
C8–C9	1.4426	N7–C8–C13	125.9
C9–C10	1.3886	N7–C8–C9	114.9
C10–C11	1.4134	C8–C9–C10	120.2
C11–C12	1.4165	C9–C10–C11	119.6
C12–C13	1.3882	C10–C11–C12	121.2
C13–C8	1.4444	C11–C12–C13	120.2
C1–H14, C10–H20, C4–H17, C13–H23	1.0973	**D(C4–C5–N7–C8)**	**24.5**
C2–H15, C11–H21	1.0988		
C3–H16, C12–H22	1.0976		
C6–H18, C9–H19	1.0974		

compounds.[48] In a round-bottom flask (200 mL), 2-aminofluorene (1.81 g, 10 mmol) was dissolved in water (40 mL) containing concentrated sulfuric acid (10 mL). The solution was cooled to below 5 °C in an ice bath and diazotized with a solution of $NaNO_2$ (0.76 g, 11 mmol) in distilled water (7 mL). The reaction was stirred in an ice bath for one hour, and occasionally small portions of water were added to rinse the walls of the flask. Then, NaN_3 (1.34 g, 20 mmol) in water (10 mL) was added at 0 °C. After 10 min, water (70–80 mL) at 0 °C was added, and the resulting suspension of solid was filtered to isolate product (1.56 g), which can be purified by recrystallization in ethanol.



Scheme 1. Diagrams of the 2-fluorenylnitrenium (top), 4-biphenylylnitrenium (middle), and diphenylnitrenium (bottom) ions with their atoms numbered as given in Table 2.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.73$ (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.29 (m, 1H), 7.21 (s, 1H), 7.02 (m, 1H), 3.89 (s, 2H); IR (film): $\tilde{\nu} = 2113$, 1604, 1581, 1454, 1401, 1307, 1292, 1281, 838, 766, 732 cm^{-1}; MS (EI): m/z (%): 179 ($C_{13}H_9N^+$, 100), 152 (24), 111 (27), 97 (45), 85 (53), 77 (73), 71 (58).

4-Azidobiphenyl: The compound 4-azidobiphenyl was also synthesized based on procedures previously reported for the synthesis of azido compounds.[48] In a round-bottom flask (200 mL), 4-aminobiphenyl (6.09 g), directly purchased from Sigma, was dissolved in water (50 mL) containing concentrated sulfuric acid (45 mL). The solution was cooled to below 5 °C in an ice bath and diazotized with a solution of sodium nitrite (2.48 g) in water (10 mL). The reaction was stirred in an ice bath for one hour, and occasionally small portions of water were added to rinse the walls of the flask. Then, sodium azide (4.23 g) in water (52 mL) was added at 0 °C. After 30 min, ice water (70–80 mL) was added, and the resulting suspension solid was filtered to isolate the product, which can be purified by recrystallization in ethanol.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.57$ (t, $J = 7$ Hz, 4H), 7.44 (t, $J = 7$ Hz, 2H), 7.34 (t, $J = 7$ Hz, 1H), 7.09 (d, $J = 9$ Hz, 2H); IR (film): $\tilde{\nu} = 1483$, 1516, 1611, 2095, 2257, 3032, 3358, 3433 cm^{-1}; MS (EI): m/z (%): 167 ($C_{12}H_9N^+$, 50); UV/Vis (MeCN): 278 nm.

N-(Diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate: The compound 1,1-diphenylhydrazine hydrochloride (2.38 g, 0.0108 mol) was dissolved in water (50 mL). Then NaOH solution (0.5 M) was added until the pH value reached about 10. The solution was then extracted three times with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to remove all solvents. The resulting product was added to a stirred solution of 2,4,6-trimethylpyrylium tetrafluoroborate (2.16 g, 0.0103 mol) in EtOH (50 mL). The reaction was refluxed for 1 h. The resulting reaction mixture was allowed to cool to room temperature. This was then cooled by an ice bath and then added to cold diethyl ether (400 mL). The crystals were filtered and washed with copious amounts of EtOH (95 %), followed by Et_2O. The crystals were dried in vacuo and weighed (3.57 g, 92 %). The product was proved to be of high purity by NMR and was not purified further.

m.p. 165–167 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.85$ (s, 2H), 7.41 (m, 4H), 7.19 (m, 4H), 6.91 (d, 2H), 2.71 (s, 3H), 2.59 (s, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 162.4$, 157.8, 140.1, 130.7, 130.6, 125.3, 117.6, 22.3, 20.1; UV/Vis (CH_3CN): 269, 373 nm.

Caution: The azide precursor compounds are potentially explosive (especially if allowed to dry) and should be handled with care.

Computational methods: All of the density functional theory computations reported here employed the Gaussian98W program suite.[49] Complete geometry optimization and vibrational frequency calculations were accomplished analytically using the BPW91 method for the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions.[50, 51] The cc-PVDZ basis set[52] was used for all of the computations.

Transient-resonance Raman spectroscopy: Samples of the precursor compound (2-azidofluorene or 4-azidobiphenyl) were made up with concentrations in the 3–5 mM range in a 75 % water/25 % acetonitrile mixed solvent by volume system with a acetate buffer (2 mM) and a pH of 3.5. The transient-resonance Raman spectra were acquired using an experimental apparatus and methods previously described,[33, 53–57] and only a short description will be given here. The excitation wavelengths for the transient-resonance Raman experiments were obtained from the harmonics of a pulsed Nd:YAG laser (GCR-150-10) and their hydrogen Raman-shifted laser lines (266 nm for the pump and 416 nm for the probe laser beams). An optical delay of about 10 ns was used between the pump and probe laser beams. The pump and probe beams were lightly focused onto a flowing liquid stream of sample using a near collinear and backscattering geometry. Reflective optics were used to collect the Raman-scattered light and image it through a depolarizer and entrance slit of a 0.5 meter spectrograph. The spectrograph grating dispersed the Raman light onto a liquid nitrogen cooled CCD (close-coupled device) mounted on the exit port of the spectrograph. The Raman signal was collected for ≈300 to 600 s before being sent to an interfaced PC computer for further analysis. About 10 to 20 of these readouts were summed to obtain a resonance Raman spectrum. Pump-only, probe-only, and pump–probe spectra were recorded. A background scan of ambient light was also collected. The known Raman bands of the water/acetonitrile solvent were used to calibrate the Raman shifts of the spectra. The solvent and precursor Raman bands were removed from the pump–probe spectrum by subtracting a probe-only Raman spectrum. The pump-only and background scan scans were also subtracted to delete any stray light or ambient light features in order to obtain the transient-resonance Raman spectra of the 2-fluorenylnitrenium, 4-biphenylylnitrenium, and diphenylnitrenium ions shown in Figure 1.

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