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ORIGINAL PAPERS

# Photochemical generation and characterization of the 5-endo-10,11-dihydrodibenzoazepine nitrenium ion

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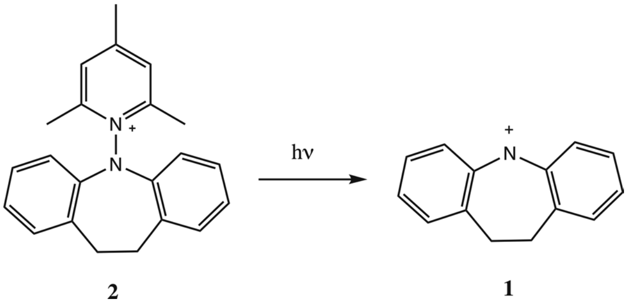
## Abstract

A photochemical precursor to the 5-endo-10,11-dihydroazepine nitrenium ion (**1**) was synthesized and used to characterize the intermediate by laser flash photolysis and stable product analysis. In addition, DFT calculations were carried out on the nitrenium ion. These results were compared with earlier studies on the diphenylnitrenium ion in order to ascertain the effect of the 2 carbon bridge on the reactions and properties of **1.** It is shown that the geometric constraints provided by the bridging group (a) destabilize the triplet state of **1** relative to the singlet state (b) substantially increase the lifetime of **1** relative to $\mathbf{Ph_2N^+}$ by inhibiting the unimolecular cyclization pathway possible in the latter and (c) modestly increases the barrier for nucleophilic addition to the ring carbons.

### Graphical abstract



## 1 Introduction

Nitrenium ions ($R_2N^+$) are reactive intermediates that feature a di-coordinate and positively charged nitrogen atom [1–4]. Arylnitrenium ions ($PhNH^+$ and substituted analogs) have been extensively studied over the past several decades, both experimentally and through computational methods. Interest in these intermediates can be attributed to the role of arylnitrenium ions in DNA damaging reactions [3, 5–13], but also because of potential applications as electrophilic nitrogen species in synthetic reactions [14–24], photoaffinity agents, as well as interest in their carbene-like electronic structure [24–32].

In general arylnitrenium ions react with alcohols, halide ions and water through addition of the latter to the ring, rather than the formally positively charged nitrogen [33–38]. However, electron-rich arenes, including the DNA base, guanine, can also provide N-adducts in certain situations. Other reactions include H-atom or hydride donation to the nitrogen center as well as electron transfer from readily oxidized donors. One interesting trend is that para-substitution on the aryl ring attenuates arylnitrenium reactivity toward oxygen centered nucleophiles, without significantly affecting the rate at which arenes react at the N center [26, 33, 39–41] (Scheme 1).

Simple arylnitrenum ions have singlet ground states due to delocalization of the charge from the nitrogen into the

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This paper is dedicated to Professor Angelo Albini on the occasion of his 75th birthday.

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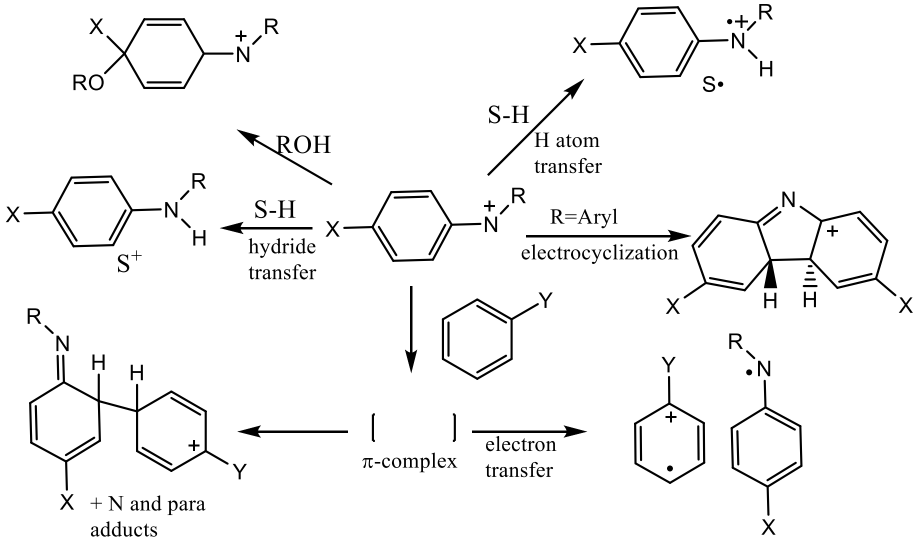


**Scheme 1** Typical reactions of arylnitrenium ions

aromatic ring. However, calculations predict that the states can be inverted when sufficiently electron-withdrawing substituents are included in the ring and/or the C–N–C central bond angle is large [1, 42–44]. Alternatively nitrenium ions with strongly donating meta substituents also can have triplet ground states [25, 45, 46]. In these cases the triplet state results from an electronic structure that involves formal transfer of an electron from the donor to the nitrogen center, creating a non-disjoint diradical ion state, analogous to the meta-xylylene diradical.

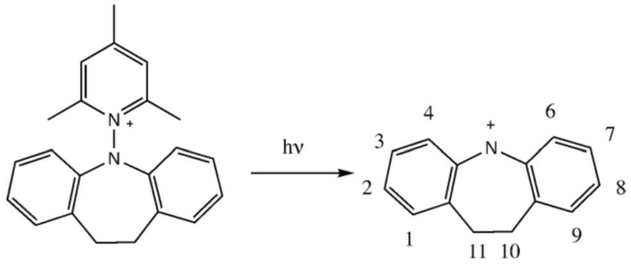
The N,N-diarylnitrenium ions, like diphenyl nitrenium ion (e.g. $Ph_2N^+$) show similar reactivity to the monoaryl series. However, there is an additional decay pathway available to the diaryls that involves electrocyclization, ultimately leading to the formation of carbazole derivatives [38, 47]. The ability of the second ring to destabilize the (nominally) $sp^2$ orbital on nitrogen by rotating out of plane, tends to decrease the singlet–triplet gap by ca. 10 kcal/mol relative to phenylnitrenium ion (ca. 20 kcal/mol), although in most cases the diaryls have singlet ground states.

As part of a long term effort to understand the effects of structure on the behavior of nitrenium ions, the current study was aimed at the 5-endo-10,11-dihydrodibenzoazepine nitrenium ion **1**. This species differs from $Ph_2N^+$ in having a two-carbon bridge that connects the arylrings at their respective ortho positions. It was anticipated that this feature would inhibit the electrocyclization leading to carbazole, leading to a longer lifetime. The weakly electron donating alkyl groups in the ortho-position were also expected to inhibit reaction with external nucleophiles, such as $H_2O$ and methanol. For the singlet–triplet energy splitting there are two competing effects. The increased C–N–C bond angle enforced by the bridge would tend to stabilize the triplet state relative to the singlet. On the other hand, the bridge is also expected to keep the two aromatics rings nearly coplanar. This effect would tend to destabilize the triplet state.

A combination of calculations, photoproduct analysis, and laser flash photolysis experiments were, therefore, carried out on 1-(10,11-dihydro-dibenzo[*b*,*f*]azepin-5-yl)-2,4,6-trimethylpyridin-1-ium tetrafluoroborate **2**, and the intermediate created from its photolysis, nitrenium ion **1** (see Scheme 2). These studies show that **1** (a) has a singlet ground state with a more substantial energy gap than that of $\mathbf{Ph_2N^+}$ (b) has a significantly longer lifetime than $\mathbf{Ph_2N^+}$ due to inhibition of the electrocyclization reactions, and (c) shows a modest decrease in reactivity toward both hydroxylic and aromatic nucleophiles.

## 2 Results and discussion

Calculations, using density functional theory (DFT – (u) M062x/6-311G(d,p)), were used to predict the geometries and electronic characteristics of nitrenium ion **1**. To the extent experimental data are available, DFT methods have been shown to provide reasonably accurate predictions of geometries, spectra, and singlet–triplet energy gaps for



**Scheme 2** Photochemical generation of 5-endo-10,11-dihydrodibenzoazepine nitrenium ion. **1**

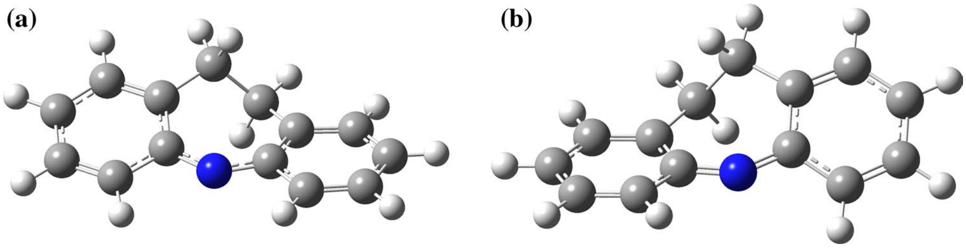


**Fig. 1** DFT-calculated geometries for (**a**) singlet and (**b**) triplet **1**

**Table 1** Comparison of DFT calculated geometries and electronic properties of **1** and $Ph_2N^+$

| | **1** | $Ph_2N^+$ |
|---|---|---|
| $\Delta E_{st}$ (kcal/mol) | − 18.5 | − 10.0 |
| $\lambda_{max}$ (nm) | 385 (s) 487 (w) 618 (w) | 353 (s) 502 (w) 645 (s) |
| Singlet C–N–C angle (deg) | 132.4 | 124.4 |
| Singlet Aryl dihedral (deg) | 20.6 | 31.2 |
| Triplet C–N–C angle (deg | 144.4 | 147.0 |
| Triplet Aryl dihedral | 34.8 | 74.6 |

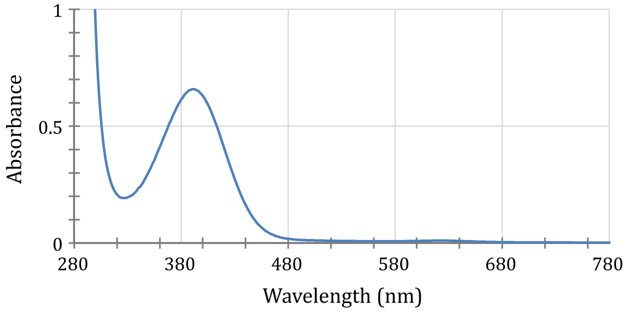


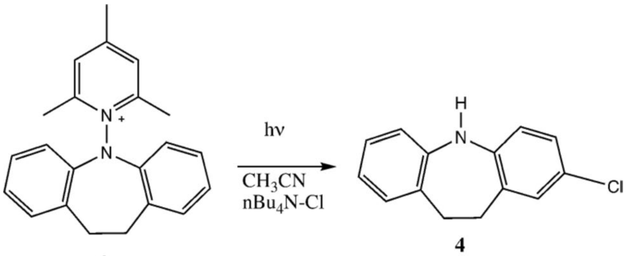
**Fig. 2** UV–Vis absorption spectrum of **2** in $CH_3CN$

carbenes, nitrenium ions and related reactive intermediates [49–52]. Minimized geometries for the singlet state and the triplet state are illustrated in Fig. 1. The singlet state shows a central (C–N–C) bond angle of 132.4 deg and the aryl rings deviate from coplanarity by 20.6 deg. The triplet, which lies 18.5 kcal/mol above the singlet, shows a larger central angle of 144.4 deg and the aryl rings are 34.8 deg away from coplanarity.

The effect of the 2-carbon bridge can be assessed by comparing these geometric parameters to those of the unconstrained diphenylnitrenium ion (**$Ph_2N^+$**). In the latter case, the singlet state shows a slightly more acute bond angle of 124.4 deg, as well as a slightly larger deviation from planarity. A more dramatic example is seen with the triplet state. The bridge forces triplet **1** to lie closer to co-planarity (34.8 deg), whereas in the unconstrained diphenyl system the rings are nearly perpendicular (74.6 deg). Similarly, the $Ph_2N^+$ triplet state can adopt a C–N–C bond angle of 147 deg (Table 1).

In all, the 2-carbon bridge distorts, and presumably destabilizes, the triplet state far more than it does the singlet state. For that reason the singlet–triplet gap increases from − 10.0 kcal/mol in **$Ph_2N^+$** (favoring the singlet) to − 18.5 kcal/mol for **1** as a consequence of the greater ring strain on the triplet.

The photochemical precursor to **1** is the N-amino-pyridinium ion **2**. The latter was prepared from 10,11-dihydro-dibenzoazepine **3** by subjecting that compound to nitrosation, reduction and condensation with 2,4,6-trimethylpyrillium tetrafluoroborate, following a previously described approach [44, 47]. The identity of the product was confirmed by standard spectroscopic methods. Characterization data and detailed procedures are provided in the supporting information. The UV–Vis spectrum of the compound is provided in Fig. 2. Similar to other examples of N-aminopyridinium ions, **2** shows a high wavelength absorption maximum in the near UV at 395 nm.



**2**

**4**

**Scheme 3** Trapping of nitrenium ion **1** with chloride

Consistent with previous examples, photolysis of the current pyridinium salt **2** generates stable products consistent with the formation of a short-lived nitrenium ion. For example, photolysis (390 nm) of **2** with tetra(n-butyl)ammonium chloride in $CH_3CN$ provides the corresponding adduct **4** that would result from nucleophilic addition to the 2-position (i.e. *para* to the nitrogen) followed by a net 1,5 hydrogen shift. This product was isolated by column chromatography and characterized by standard spectroscopic methods (See Scheme 3).

Similarly, photolysis (370 nm) of the pyridinium ion **2** in $CDCl_3$ solutions containing 1,4-cyclohexadiene (CHD, a reactive H atom donor) were photolyzed. Product analysis by

$^1$H NMR spectroscopy showed clean formation of the corresponding amine, accompanied by benzene (from oxidation of the 1,4 cyclohexadiene). Below will be presented spectroscopic evidence supporting a stepwise H atom transfer mechanism for this process (Scheme 4).

Laser flash photolysis experiments were used to characterize the nitrenium ion intermediate. Shown in Fig. 3 are transient spectra measured following pulsed laser excitation (355 nm, 7 ns, 40 mJ) of pyridinium ion **2** in $CH_3CN$ solution. A strong absorbance with an apparent maximum of 450 nm appears immediately following the excitation pulse and decays in a kinetically complex manner, persisting for over 100 µs following the excitation pulse. A nearly identical spectrum and decay profile were also obtained in $CH_2Cl_2$.

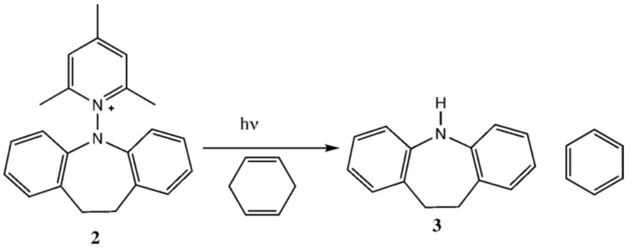
The assignment of the signal to nitrenium ion **1** is supported by the following observations: (1) The 450 nm decay profile is not significantly changed when the experiment is carried out with $N_2$ saturated or air-equilibrated solutions. Generally speaking aryl and diarylnitrenium ions, being ground state singlets, are unreactive toward oxygen. (2) The lifetime of the 450 nm signal, however, is diminished when nucleophiles known to react with similar arylnitrenium ions such as chloride ions, and methanol are added to the solution (see Table 2). (3) The transient spectrum in Fig. 3 shows reasonable agreement with a UV–Vis spectrum calculated by time-dependent density functional theory (TD-DFT) (Fig. 3). The latter predicts a significant peak at 395 nm and a weaker absorption at 618 nm. It should be noted that the transient spectrum in Fig. 3 is a difference spectrum. Depletion of the photoprecursor **2** at 405 nm (see Fig. 1) subtracts from the positive signal for the photoproduct. Thus, the true experimental maximum could be at significantly lower wavelengths than the apparent maximum at 450 nm.

The substantially increased lifetime of **1** compared to $\mathbf{Ph_2N^+}$ and other diarylnitrenium ions can be attributed to the inhibition of the electrocyclization reaction. Under

**Table 2** Rate constants for reactions of nitrenium ion **1** in $CH_3CN$ with various trapping agents determined by LFP

| Trapping agent | $k_{trap}$ ($M^{-1}$ $s^{-1}$) |
|---|---|
| $Bu_4NCl$ | $2.57\times10^{10}$ |
| MeOH | $5.46\times10^{5}$ |
| $H_2O$ | $3.97\times10^{4}$ |
| AMP | $4.46\times10^{7}$ |
| GMP | $9.60\times10^{7}$ |
| L-Cysteine | $3.95\times10^{8}$ |
| L-Tryptophan | $2.52\times10^{9}$ |
| L-Methionine | $8.63\times10^{8}$ |
| L-Tyrosine | $2.10\times10^{7}$ |
| L-Arginine | $6.49\times10^{7}$ |
| L-Lysine | $3.72\times10^{7}$ |

*AMP* adenosine monophosphate, *GMP* guanosine monophosphate



**Scheme 4** Reductive trapping of nitrenium ion **1** using 1,4-cyclohexadiene

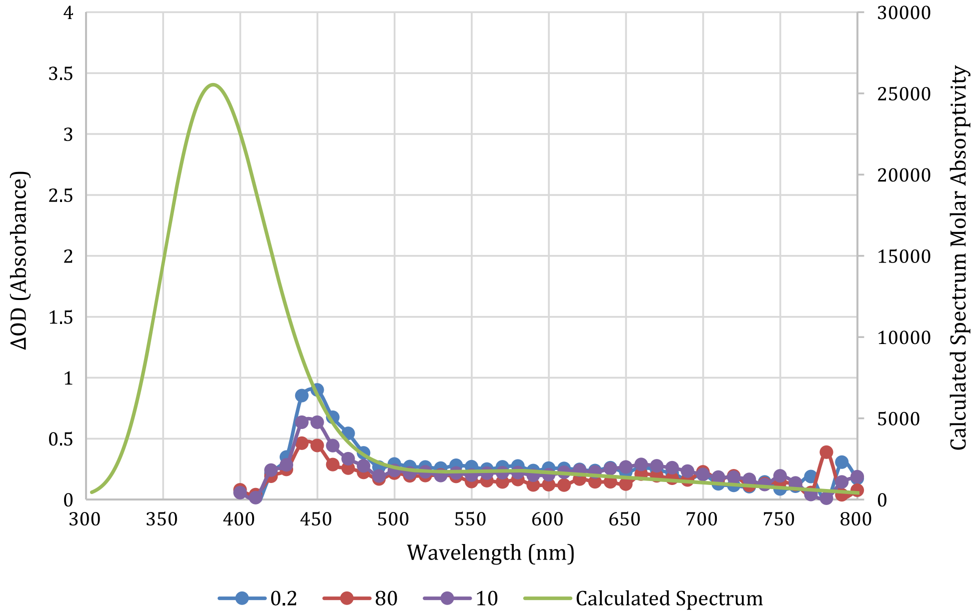


**Fig. 3** Transient spectra from laser flash photolysis (355 nm, 7 ns, 40 mJ/pulse) of pyridinium ion **2** in $CH_3CN$ solution taken 200 ns, 10 µs, and 80 µs following the excitation pulse. This difference spectrum should give the absorption spectrum of **1** which can be compared to the TD-DFT modeled UV–Vis spectrum of **1**

comparable conditions, $\mathbf{Ph_2N^+}$ lives for ca. 1.5 μs and has been shown to produce carbazole along with oligomeric species when generated in the absence of added nucleophiles. Generation of **1** under similar conditions also generates complex colored mixtures which we assume to result from oligomerization processes similar to what was reported previously [38, 44]. However, no product analogous to carbazole was identified.

The reactivity of nitrenium ion **1** was ascertained by measuring the dependence of the pseudo-first-order decay rate constants $k_{obs}$ on the concentrations of the various trapping agents [Trap] listed in Table 2. In all cases the rate constants agreed reasonably well with Eq. (1), where $k_0$ reflects the projected decay rate constant absent the trap and $k_{trap}$ is the second order rate constant:

$$k_{obs} = k_0 + k_{trap}[\text{Trap}] \qquad (1)$$

A general trend that emerges from these rate data is the diminished reactivity of nitrenium ion **1** toward typical nucleophiles. For example, the rate constant of reaction with water is ca. $4 \times 10^4$ $M^{-1}$ $s^{-1}$, which about 20 times slower than the reaction of $Ph_2N^+$ with the same nucleophile ($6.1 \times 10^5$ $M^{-1}$ $s^{-1}$) [44]. In contrast the electron rich amino acid, tryptophan, reacts at near the diffusion limit in $H_2O$ with both nitrenium ions. This effect is similar to the reactivity of the para-substituted dihalo-diphenyl nitrenium ions with $H_2O$. The most electrophilic position on the diarylnitrenium ions is the para position, but the rate constant of the reaction with water is the same order of magnitude for **1** as well as for the para-dihalo-diphenyl nitrenium ions. Therefore, the decreased rate constant with of the reaction with water is primarily due to restricting one of the electrophilic ortho sites on the aryl rings.

Calculations (M062x/6-311G(d,p) including implicit $CH_3CN$ solvation simulated using the SMD model) on the transition states for addition of water to **1** and $\mathbf{Ph_2N^+}$ are consistent with the experimental trends (Fig. 4). The Gibbs free energy of activation for addition of $H_2O$ to **1** is 8.6 kcal/mol, this is ca. 2 kcal/mol higher than that for addition to $\mathbf{Ph_2N^+}$ (6.4 kcal/mol). However, it should be noted that in both cases the addition reactions are expected to be endergonic. However, under experimental conditions these can occur with concerted deprotonation to other water molecules resulting in the net exergonic addition of hydroxide. More extensive simulations using explicit solvent molecules would be needed to quantitatively model this reaction.

Nitrenium ion **1** reacts with the H atom donor, 1,4-cyclohexadiene (CHD), with a rate constant of $1.8 \times 10^5$ $M^{-1}$ $s^{-1}$. LFP experiments show that this reaction happens through a H atom transfer mechanism. Figure 5 shows transient spectra taken following LFP of **2** in the presence of 0.5 M of CHD. Following the decay of the nitrenium ion signal (450 nm) there appears weaker, but persistent, signals at 520 nm and 690 nm. These agree well with the transient spectrum of the **3** cation radical generated

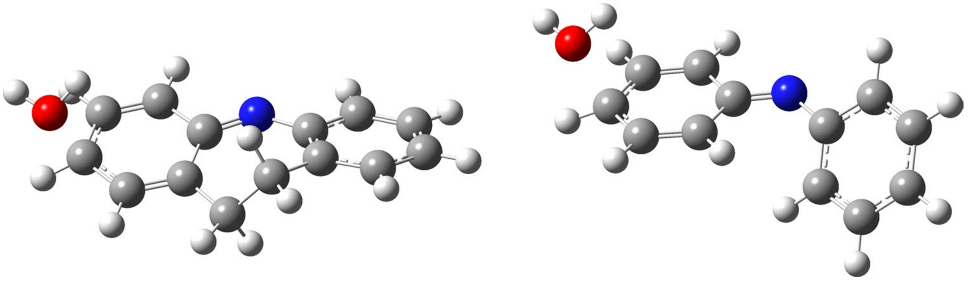


**Fig. 4** Transition state geometries (M062x/6-311G(d,p)-SMD) for addition of $H_2O$ to **1** and $\mathbf{Ph_2N^+}$ in $CH_3CN$

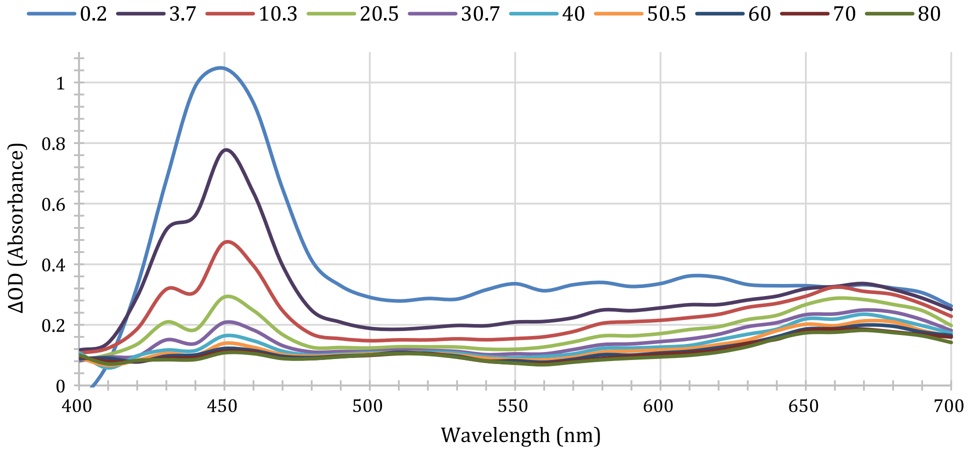


**Fig. 5** Transient spectra resulting from LFP (355 nm, 7 ns, 40 mJ) of **2** and 1,4-cyclohexadiene in $CH_3CN$

independently (SI1). Furthermore, the rate constant of **1** with CHD is around 20 times lower than the rate constant of diphenyl nitrenium ion with CHD or the dihalo-diphenyl nitrenium ions with CHD. This would suggest that although **1** is similar to the dihalo-diphenyl nitrenium ions in regards to its reactivity to nucleophiles, it has a greater difference in its 2nd order rate constants with H-atom donors than do the dihalo-diphenyl nitrenium ions. This is evidence that indeed the triplet state of the nitrenium ion is destabilized for **1** in comparison to diphenyl nitrenium ion, but the reactivity of the singlet state is approximately the same as the dihalo-diphenyl nitrenium ions as measured through 2nd order rate constants with different nucleophiles.

Previous studies of other diarylnitrenium ions have shown some level of radical cation formation under certain conditions [48]. These have been attributed to reactions of nitrenium ion triplet states and/or branching from the initially formed pyridinium excited states. This example further establishes this pathway in a case where the nitrenium ion triplet state is even more energetically separated from the singlet. The large $\Delta E_{st}$ value for **1** tends to exclude H atom transfer via the equilibrated triplet state. One possibility is that the singlet abstracts H atoms directly. Additional studies would be needed to test this hypothesis.

## 3 Conclusions

When comparing nitrenium ion **1** to $\mathbf{Ph_2N^+}$, the most significant effect of the saturated two-carbon bridge is to destabilize the triplet state relative to the singlet, further increasing the singlet–triplet energy gap ($\Delta E_{st}$). Analysis of the geometries shows that the second ring in the $\mathbf{Ph_2N^+}$ is able to rotate out of planarity and destabilize the filled $sp^2$ non-bonded orbital on nitrogen. The bridge makes this impossible and the two aryl rings lie nearly coplanar. The bridge significantly extends the lifetime of **1** by inhibiting the electrocyclization reaction leading to carbazole in the case of **1.** The bridge also shows a modest effect on reaction with nucleophiles, inhibiting the addition of $H_2O$ to the ring by ca. a factor of 10. This supports the idea that singlet state of **1** is not greatly affected by the two-carbon bridge as its reactivity with nucleophiles is not greatly affected.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s43630-022-00267-3.

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## Declarations

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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