Communication

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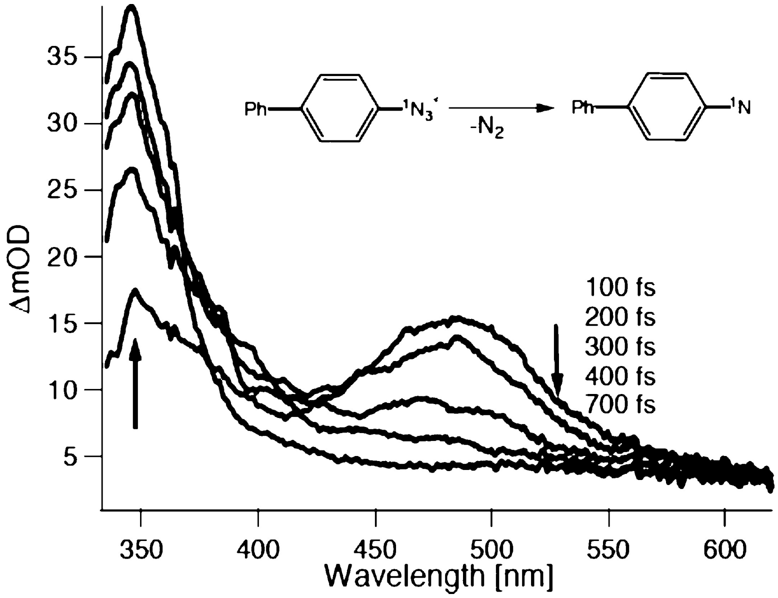

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The Direct Detection of an Aryl Azide Excited State: An Ultrafast Study of the Photochemistry of *para*- and *ortho*-Biphenyl Azide

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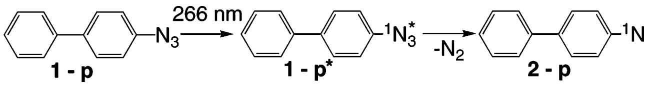
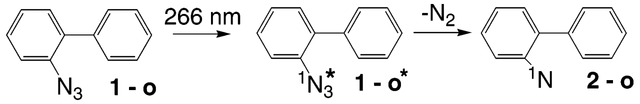
Photolysis of aryl diazo compounds and azides produces carbenes and nitrenes, respectively, which have received extensive study by nanosecond (ns) time-resolved spectroscopy and other physical methods.[1−3] The excited states of aryl diazo compounds have been recently detected by femtosecond spectroscopy.[4] Herein, we report the first observation of aryl azide excited singlet states and the formation of the related singlet nitrenes.

In the femtosecond transient absorption experiments, the azides were excited at 266 nm and monitored with a supercontinuum probe pulse in the spectral range of 335−625 nm. The recorded spectra were time-corrected for the chirp of the supercontinuum.[5] The time resolution of the system is 300 fs, as determined by the two-photon absorption of methanol in the sample cell.

The *para*- and *ortho*-biphenyl azides were chosen for initial study because of their prior study by nanosecond spectroscopy. Laser Flash Photolysis (LFP) of *para*-biphenyl azide in acetonitrile produces the singlet nitrene with $\lambda_{max} = 350$ nm and $\tau \sim 9$ ns at ambient temperature.[6]



Singlet *ortho*-biphenylnitrene has a sub-nanosecond lifetime at ambient temperature. LFP of *ortho*-biphenyl azide at 77 K in glassy 3-methylpentane produces a singlet nitrene with $\lambda_{max} = 410$ nm and $\tau = 59$ ns under cryogenic conditions.[6]



Ultrafast LFP of **1-p** (o.d. = 0.6 at 266 nm) in acetonitrile at ambient temperature produces the transient spectra shown in Figure 1. There is a broadly absorbing transient at 480 nm that forms within the laser pulse (Figure 1 inset) and decays with a time constant of ∼100 fs. As the transient absorption decays at 480 nm, it grows at 350 nm. The latter species is readily assigned to **2-p** on the basis of nanosecond time-resolved studies. The precursor of the singlet nitrene is an excited state of the azide **1-p**, which absorbs at 480 nm.

As expected, relaxed singlet nitrene (**2-p**) does not exhibit any significant population decay on the 100 ps time scale. The transient absorption spectrum, however, of the singlet nitrene (**2-p**) undergoes subtle reshaping within a few picoseconds of the laser pulse. A decay (11 ps) is observed on the red edge (380 nm) of the absorption band. This pattern is characteristic of vibrational cooling (VC) of species initially formed with excess vibrational energy.[7] The 11 ps time constant is consistent with other reports of VC of polyatomic molecules.[8] A derivative of **2-p**, 3,5-dichloro-*ortho*-biphenylnitrene, also undergoes vibrational cooling in cyclohexane with an 11 ps decay time.[9]

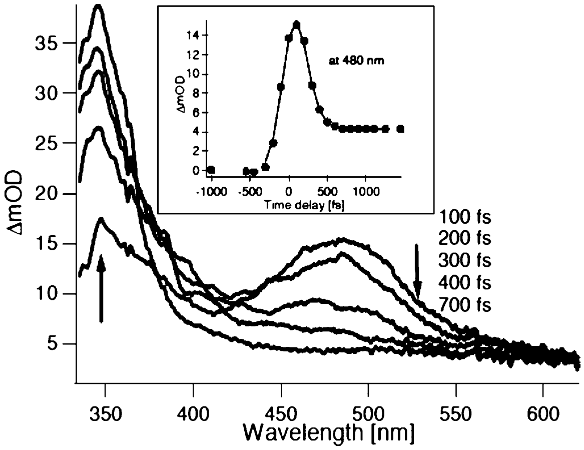


Figure 1. Transient absorption spectra recorded in a 100−700 fs time window for *para*-biphenyl azide in acetonitrile. The time dependence of the signal at 480 nm is shown in the inset.

Ultrafast LFP of *ortho*-biphenyl azide **1-o** in acetonitrile (o.d. = 0.6 at 266 nm) at ambient temperature produces the transient spectra of Figure 2. Transient absorption at 480 nm (^{1}**1-o***) is formed within the laser pulse and decays with a time constant of 450 ± 150 fs (Figure 2a inset). As this absorption decays, a new absorption at 400 nm (**2-o**) grows with a time constant of 280 ± 150 fs. Singlet *ortho*-biphenylnitrene decays with a time constant of 16 ± 3 ps (Figure 2b inset). The 16 ps time constant represents the population decay time of the singlet nitrene (**2-o**) by isomerization to isocarbazole and a benzazirine (and subsequently the ring expands to form a 1,2-didehydroazepine). There is an isosbestic point at 435 nm. This is the first observation of singlet *ortho*-biphenylnitrene in solution at ambient temperature. Its lifetime is shorter than that of singlet 3,5-dichloro-*ortho*-biphenylnitrene[9] (260 ps, cyclohexane; 62 ps, methanol; $\lambda_{max} = 425$ nm).

Vertical excitations and full geometry optimizations were performed for the different states (S_0, S_1, and S_2) of *p*-biphenyl azide using the hybrid B3LYP[10] density functional theory method and the TZVP basis set[11] as implemented in Turbomole 5.71.[12] The S_1 and S_2 excited states were optimized using time-dependent DFT methodology. Vertical excitations from $S_0 \rightarrow S_1$ and from $S_0 \rightarrow S_2$ were computed to occur at 287 and 272 nm, respectively, using the more flexible Sadlej basis set,[13] and the former band is predicted

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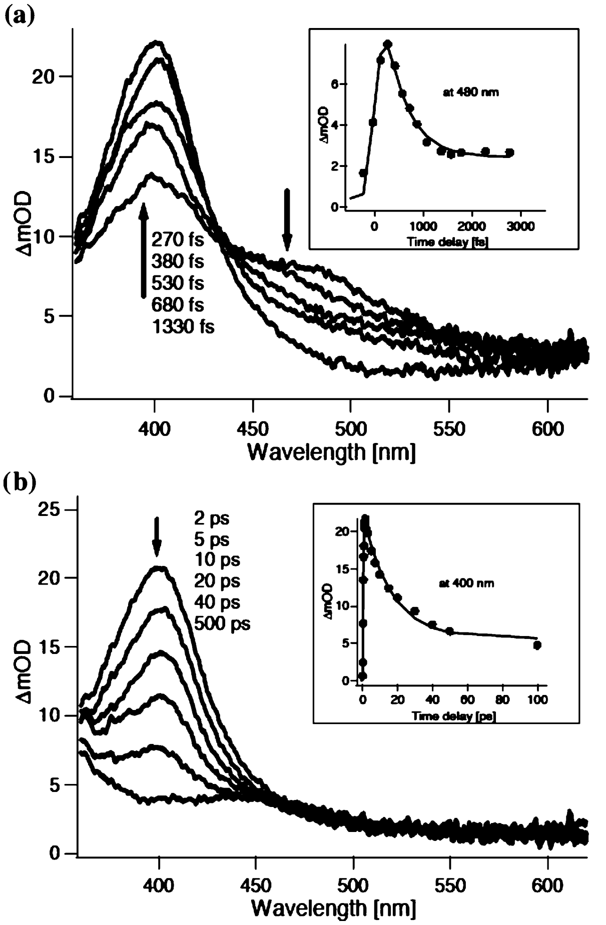

Figure 2. Transient absorption spectra recorded between (a) 270−1330 fs after the laser pulse and with (b) 2−500 ps time windows for *ortho*-biphenyl azide in acetonitrile. The time dependences of the signal measured at 480 and 400 nm are shown as insets.

to have a significant oscillator strength ($f = 0.66$). The geometry of S_1 is computed to be dissociative to generate *p*-biphenylnitrene and N_2. Indeed, optimization attempts for S_1 lead to convergence difficulties as the ArCN−N_2 bond length is elongated toward formation of molecular nitrogen. The S_2 state, however, is bound with a ArCN−N_2 bond length of 1.252 Å, similar to the 1.228 Å value for S_0. Both S_0 and S_2 were confirmed to be minima by evaluation of the Hessian matrix, and each state had only real vibrational frequencies. Thus, we assign the initially detected transient to the S_2 state of *para*-biphenyl azide.

In summary, aryl azide excited singlet states have been observed for the first time. Their short (femtosecond) but finite lifetimes indicate that these excited state surfaces are not purely repulsive. Aryl azide excited states decompose to form singlet aryl nitrenes whose growth can be observed by ultrafast spectroscopy.

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