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An ultrafast time-resolved infrared and UV-vis spectroscopic and computational study of the photochemistry of acyl azides

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The photochemistry of pivaloyl, benzoyl, 4-phenylbenzoyl, and 2-anthroyl azides has been studied using femtosecond (fs) time-resolved infrared (TRIR) and UV-vis spectroscopy and interpreted with the aid of computational chemistry. Density functional theory calculations revealed a significant difference in the nature of the lowest singlet excited state for these carbonyl azides. The lowest singlet excited states (S_1) of *p*-phenylbenzoyl and 2-anthroyl azides are (π, π^*) in nature, while the pivaloyl and benzoyl azides S_1 states involve (n, π^*) excitations. Nevertheless, for all acyl azides studied here, a similar, and intense, IR band at about 2100 cm^{-1} has been detected in the ultrafast TRIR experiments following 270 nm excitation. These bands were shifted to lower energy by about 100 cm^{-1} relative to the N_3 stretching mode for the ground states of these azides. These 2100 cm^{-1} vibrational bands were assigned to the S_1 states of acyl azides in agreement with density functional theory calculations. The decay of the acyl azide S_1 states was described by bi-exponential functions. The fast component was attributed to the decay of the hot S_1 state and the longer component to the decay of the thermally relaxed S_1 state. A strong and broad transient absorption in the 350–650 nm spectral range was observed in the fs UV-vis experiments for *p*-phenylbenzoyl and 2-anthroyl azides. The carrier of this absorption also decayed bi-exponentially, and the time constants were in excellent agreement with those found in the fs TRIR experiments. The slow component of the S_1 state decay was found to be dependent on the solvent polarity. When the lifetime of the acyl azide S_1 state is substantially longer than the time constant for vibrational cooling of nascent (hot) isocyanate, the correlation between the S_1 decay and isocyanate formation was clear. The 270 nm excitation populates the S_n ($n \geq 2$) states of these acyl azides. It was established that a hot nitrene is produced more efficiently from both the S_n and hot S_1 states than from the relaxed S_1 state of these acyl azides. Thus, time-resolved study provides direct experimental evidence that the S_1 state is the precursor of nitrene only when the S_1 state is pumped directly and when the S_1 state lifetime is longer than the time constant of vibrational cooling of the newborn nitrene. All of these results are consistent with the data obtained recently for 2-naphthoyl azide. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords: acyl azide; computational chemistry; excited state; femtosecond spectroscopy; photochemistry

INTRODUCTION

Acy azides undergo Curtius rearrangement upon either thermal or photochemical activation.^[1,2] The light-induced decomposition of pivaloyl azide produces both the corresponding isocyanate and acylnitrene.^[1,2] Physical organic chemists have explored nitrenes for several decades. Imidogen, alkyl, and aryl nitrenes are known to have triplet ground states; however, carbonylnitrenes were found to have singlet ground states in apparent violation of Hund's rule.^[3] In the seminal computational work of Pritchard and Gritsan,^[4] the closed-shell singlet states were shown to be the ground states of carbonylnitrenes. This is due to a bonding interaction between the oxygen atom of the carbonyl group and the electrophilic nitrogen atom of the nitrene, and this interaction selectively stabilizes the singlet state of the acylnitrene over its triplet state.

Nanosecond time-resolved infrared (TRIR) experiments with xanthone sensitization suggested that a singlet acyl azide excited state must be the precursor to the corresponding isocyanate.^[5] This was in agreement with the previous work of Schuster *et al.*^[6] wherein they demonstrated that *p*-acetylbenzoyl azide (containing an internal triplet sensitizer) in the triplet (n, π^*) state does not

produce isocyanate. Photolysis of 2-naphthoyl azide (2-NpCON₃) with an external triplet sensitizer also produced a negligible amount of isocyanate.^[3] Thus, these findings indicate that the singlet excited state of the acyl azide is the precursor of isocyanate. However, this conclusion was not supported by any direct, time-resolved experiments.

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Subsequently, Gritsan, Bally, Toscano, and coworkers reported nanosecond TRIR spectroscopic studies of benzoyl azide (PhCON_3)^[7] and found that isocyanate and carbonylnitrene are both formed within the time resolution of their instrument (~50 ns). In our preliminary study^[8] of PhCON_3 , 2-NpCON₃, and pivaloyl azide ($t\text{-BuCON}_3$) photochemistry, the decay of the acyl azide's singlet excited states along with formation of the singlet acylnitrenes and isocyanates was observed using femtosecond (fs) TRIR spectroscopy. This was the first direct observation of the singlet excited state of an acyl azide as well as the dynamics of its decay. The S_1 state of 2-NpCON₃ was found to have a lifetime of 120 ps in chloroform, which is consistent with that estimated by Autrey and Schuster ($\tau < 2$ ns).^[3]

Very recently, we reported the results of an fs time-resolved UV-vis and IR study^[9] of the photochemistry of 2-NpCON₃ in a series of solvents. Polar solvents were found to accelerate the S_1 state's decay significantly. It was demonstrated that upon excitation of 2-NpCON₃ directly to the S_1 state ($\lambda_{\text{exc}} = 350$ nm), this state produces singlet nitrene (2-NpCON) and isocyanate (2-NpNCO). Upon excitation at 270 nm, higher-lying singlet excited [S_n ($n \geq 2$)] states are populated. The S_n states also produce singlet 2-NpCON in competition with internal conversion to the S_1 state of the azide, where upon the 2-NpCON and 2-NpNCO are formed.

As the π -electron delocalization differs significantly in the aroyl azides under study (PhCON_3 , 2-NpCON₃, $p\text{-BpCON}_3$, and 2-AnCON₃, Scheme 1), one can expect considerable differences in their excited state manifolds. Of course, $t\text{-BuCON}_3$ does not contain an aromatic chromophore; thus, it should have very different types of excited states when compared with the aforementioned aromatic aroyl azides.

In this paper, we report results of ultrafast TRIR and UV-vis studies on the photochemistry of PhCON_3 , $p\text{-BpCON}_3$, 2-AnCON₃, and $t\text{-BuCON}_3$ (Chart 1) in chloroform and in acetonitrile, along with density functional theory (DFT) calculations. TRIR data for PhCON_3 and $t\text{-BuCON}_3$ in chloroform were published recently^[8], and they are presented here for comparison. All of our experimental findings are consistent with the predictions made by DFT calculations.

EXPERIMENTAL SECTION

Computational details

All of the calculations were performed at the Ohio Supercomputer Center using TURBOMOLE-5.91 software.^[10–12] Carbonyl azides were optimized using Becke's three-parameter hybrid exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) method,^[13,14] along with

Table 1. Vertical excitation energies, oscillator strengths, and the dominant occupied and virtual orbitals contributing to four lowest energy singlet excitations calculated at the TD-B3LYP/TZVP level of theory

State	Character (% contribution)	Energy/ eV (nm)	Oscillator strength
<i>t</i> -BuCON ₃			
S_1	34 → 35 (97)	4.56 (272)	1.3×10^{-3}
S_2	33 → 36 (98)	5.02 (247)	5.4×10^{-4}
S_3	34 → 36 (73)	5.10 (243)	1.2×10^{-3}
S_4	33 → 35 (49)	6.14 (202)	1.7×10^{-1}
PhCON ₃			
S_1	36 → 39 (98)	4.23 (293)	1.3×10^{-4}
S_2	38 → 39 (89)	4.57 (271)	1.8×10^{-2}
S_3	37 → 39 (76)	4.86 (255)	2.7×10^{-1}
S_4	35 → 40 (66)	4.97 (249)	2.4×10^{-4}
<i>p</i> -BpCON ₃			
S_1	58 → 59 (97)	4.04 (307)	5.7×10^{-1}
S_2	55 → 59 (92)	4.19 (296)	1.1×10^{-2}
S_3	57 → 59 (55)	4.46 (278)	2.0×10^{-3}
S_4	56 → 59 (51)	4.48 (277)	1.3×10^{-2}
2-AnCON ₃			
S_1	64 → 65 (97)	2.87 (432)	7.3×10^{-2}
S_2	64 → 66 (62)	3.58 (346)	1.2×10^{-2}
S_3	64 → 67 (99)	4.01 (309)	8.6×10^{-6}
S_4	61 → 65 (86)	4.08 (304)	7.9×10^{-5}

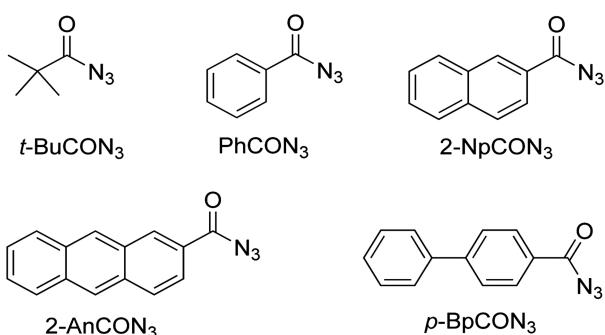
triple zeta valence polarized basis sets (TZVP),^[15] by using C_1 symmetry. Excited state calculations were performed using time-dependent B3LYP (TD-B3LYP) methodology.^[16] The geometries of the first singlet excited states of the carbonyl azides under study were optimized at the TD-B3LYP/TZVP level of theory with the exception of $t\text{-BuCON}_3$, where all of our attempts to optimize the excited state at this level of theory failed. The computational analysis for $t\text{-BuCON}_3$ was instead performed at the TD-B3LYP/SVP level of theory. The stationary points discovered on the singlet excited state surfaces were confirmed to be minima by calculating the second derivatives numerically with the NumForce module in TURBOMOLE. This approach led to the prediction of the IR spectra of the singlet excited states at the TD-B3LYP/TZVP level of theory (except $t\text{-BuCON}_3$ where the TD-B3LYP/SVP level of theory was used). For all of these calculations, a restricted formalism was used for the reference DFT wave function.

Materials

Acetonitrile and chloroform (Burdick and Jackson, spectrometric grade) were used as received. Unless otherwise noted, other materials were obtained from Sigma Aldrich Chemical Co. and used without further purification. All acyl azides under investigation are known compounds, and their syntheses have been reported previously. $t\text{-BuCON}_3$,^[17] $p\text{-BpCON}_3$,^[18] PhCON₃,^[19] and 2-AnCON₃^[20] were synthesized following the procedure described for benzoyl azide by Barrett and Porter.^{[19],[21]}

Experimental details

Ultrafast IR and UV-vis pump-probe absorption measurements were performed using home-built spectrometers at The Ohio State University. The time resolution is about 300 fs for both the UV-vis and TRIR instruments. The spectrometers are described in more detail elsewhere.^[22–24] The absorbance of the sample solutions was about 1.0 in a 1 mm cell (or less than 0.15 for $t\text{-BuCON}_3$) at the excitation wavelength. Sample solutions were excited in a stainless steel flow cell equipped with 2-mm-thick



Scheme 1. The carbonyl azides in this study

BaF_2 windows in the case of the IR instrument and CaF_2 windows (1-mm-thick front window and 2-mm-thick back window) in the case of the UV-vis instrument. After passing through the sample, the reference and probe beam were spectrally dispersed with a polychromator and independently imaged on a liquid-nitrogen cooled HgCdTe detector (2×32 pixels) (TRIR setup) and thermoelectrically cooled charge-coupled device camera (UV-vis setup). The pump pulse energy was $\leq 4\mu\text{J}$ at the sample position, and the pump beam diameter (full width at half maximum) was equal to about $250\mu\text{m}$. The entire set of pump-probe delay positions (cycle) is repeated at least three times to observe data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarization of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces were analyzed by fitting to a sum of exponential terms. All experiments were performed at room temperature.

COMPUTATIONAL RESULTS

Optimization of ground state geometries and computed vertical excitations

To understand the photochemical properties of $t\text{-BuCON}_3$, PhCON_3 , $p\text{-BpCON}_3$, and 2-AnCON_3 , we optimized their ground state geometries at the B3LYP/TZVP level of theory. Both the *syn* and *anti* conformations (around the $(\text{O})\text{C}-\text{N}(\text{N}_2)$ carbonyl azide bond, Fig. 1) were independently optimized for $t\text{-BuCON}_3$, PhCON_3 , and 2-AnCON_3 . The *syn* conformation was found to be more stable by about 7–8 kcal/mol for all of these carbonyl azides. This is attributed to the repulsion between the aromatic H and the N_3 unit for the aryl azides while, for $t\text{-BuCON}_3$, a repulsive interaction between the N_3 unit and the methyl groups of the *t*-Bu group. Thus, all of the following discussions will involve only the *syn* conformations.

Vertical excitations were calculated for the *syn* conformers of these acyl azides at the TD-B3LYP/TZVP level of theory. Transitions to the S_1 states of $p\text{-BpCON}_3$ and 2-AnCON_3 were predicted

to have large oscillator strengths indicating their (π,π^*) character because of the availability of significant π -electron density (Table 1). On the contrary, both the PhCON_3 and $t\text{-BuCON}_3$ have forbidden (n,π^*) transitions to their lowest singlet excited S_1 states. Thus, these calculations indicate that the photochemical behavior of two sets of acyl azides could be different.

To determine the character of the excited states of these acyl azides, we computed electron density difference plots for the lowest identified singlet excited states. When there is only one dominant orbital-to-orbital transition for a vertical excitation, one can examine both orbitals to identify the character of the excited state. However, if a vertical excitation is composed of multiple orbital-to-orbital transitions, it is virtually impossible to extrapolate the character of the excited state by looking at the individual orbitals. To overcome this problem, one can compute the electronic density distribution in both the ground state and the Frank-Condon excited state followed by subtraction of the ground state electronic density from the Frank-Condon excited state electronic density, thereby giving an electron density difference plot. In the recent past, we have utilized this strategy to analyze the photochemical behavior of many different chemical systems.^[25–29] For these plots, a red or green contour indicates depletion or accumulation of electronic density in the excited state relative to the ground state, respectively.

In the S_1 state of PhCON_3 , the electronic excitation is primarily localized on the carbonyl unit with a minimal amount of electronic difference density at the azide group (Fig. 2). Thus, this state is (n,π^*) in nature. On the other hand, in the lowest singlet excited state of $t\text{-BuCON}_3$, the excitation is localized both on the carbonyl and the azide groups (Fig. 3). A pronounced electronic difference density at the carbonyl unit is an indication of the (n,π^*) character. However, excitation from the in-plane π orbital of the azide unit to the out-of-plane π^* orbital contributes significantly to this transition. One should note, however, that both of

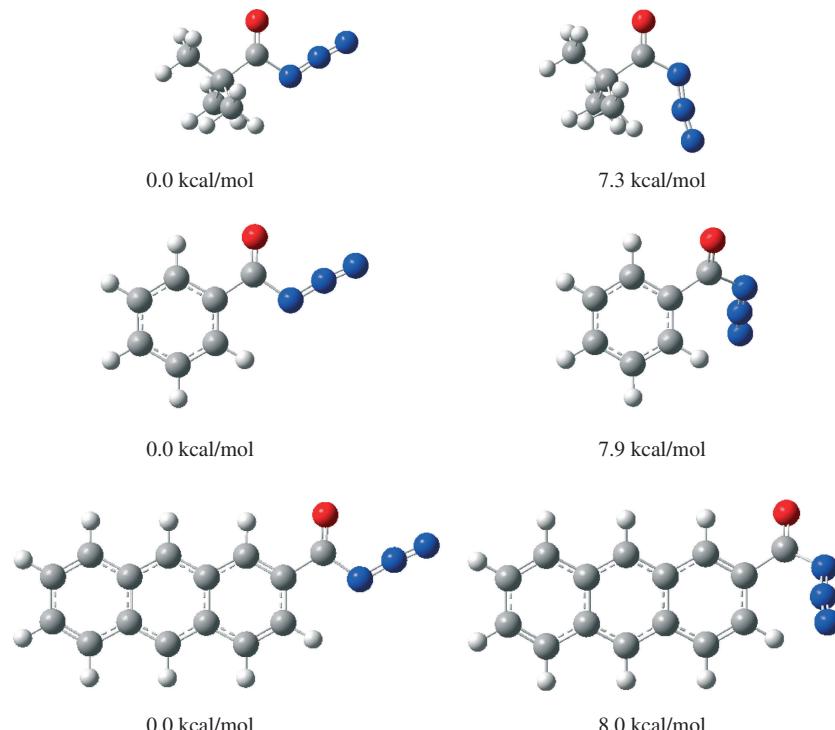


Figure 1. *Anti* and *syn* conformations of carbonyl azides and their energetics as obtained at the B3LYP/TZVP level of theory

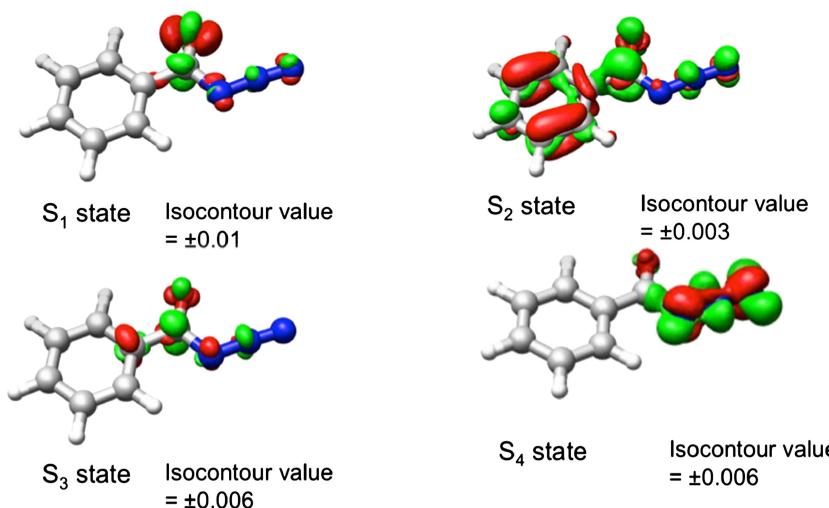


Figure 2. Electron density difference plots for the S_1 to S_4 states of PhCON_3 calculated at the TD-B3LYP/TZVP level of theory. The green contours depict the accumulation of electron density in the excited state, and the red contours illustrate the loss of electron density in the excited state

these excitations have very low calculated oscillator strengths (Table 1). The in-plane π orbital to out-of-plane π^* orbital transitions localized on the azide unit were predicted for the lowest singlet excited states of some aryl azides, including phenyl,^[30,31] *p*-biphenyl, *o*-biphenyl, and 1-naphthyl azides.^[22,32] Such an excited state was found to produce the singlet nitrene and nitrogen molecule with a very small energy barrier, which is defined as a *dissociative state*. Thus, *t*-BuCON₃ has a significant *dissociative* character in the S_1 state, while the lowest singlet excited state of PhCON₃ is primarily localized on the carbonyl unit. For PhCON₃, however, the *dissociative* state is a higher-lying excited S_4 state (Fig. 2).

Both *p*-BpCON₃ and 2-AnCON₃ have their S_1 states substantially localized on the aromatic moiety with only a small contribution from the azide group (Figs. 4 and 5). A similar difference density plot has been observed for the S_1 state of 2-NpCON₃.^[9] The (π, π^*) character of the S_1 excited state explains why both *p*-BpCON₃ and 2-AnCON₃ have high oscillator strengths for their

transitions to the S_1 state as compared with *t*-BuCON₃ and PhCON₃. For both *p*-BpCON₃ and 2-AnCON₃, the *dissociative* state is located higher in the excited state manifold, namely, in the S_2 and S_3 states, respectively. As there is considerable difference in the character of the lowest singlet excited states of these two sets of acyl azides, these compounds may have different photochemical channels leading to different products. However, as previously shown, excitation with 270-nm light for both PhCON₃ and 2-NpCON₃ in chloroform leads to the formation of the corresponding isocyanate and singlet aroylnitrene,^[8] suggesting similar photochemical behavior of these two acyl azides. The calculated difference density plots and the vertical excitation energies (Table 1) suggest differences in the excited state ordering. Nevertheless, calculations predict that 270 nm excitation leads to S_n ($n \geq 2$) states, and it is possible that S_n states could generate the intermediates observed in the ultrafast TRIR experiments. Indeed, formation of 2-naphthoylnitrene using 270 nm excitation was biphasic, indicating that two different channels

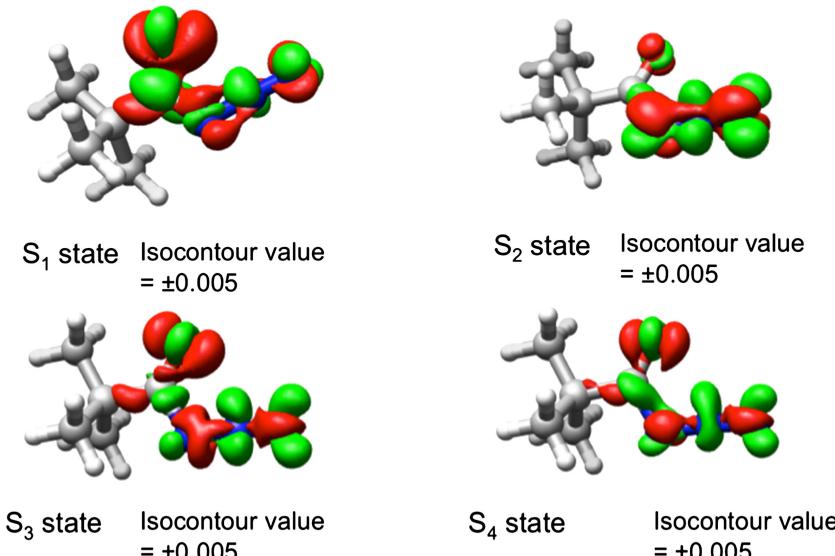


Figure 3. Electron density difference plots for the S_1 to S_4 states of t -BuCON₃ calculated at the TD-B3LYP/TZVP level of theory. The green contours depict the accumulation of electron density in the excited state, and the red contours illustrate the loss of electron density from the S_0 ground state

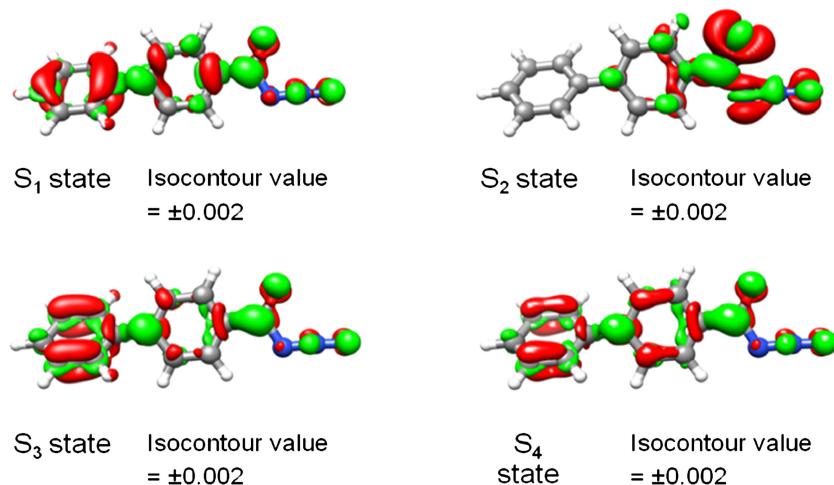


Figure 4. Electron density difference plots for the S_1 to S_4 states for $p\text{-BpCON}_3$ calculated at the TD-B3LYP/TZVP level of theory. The green contours depict the accumulation of electron density in the excited state, and the red contours illustrate the loss of electron density from the S_0 ground state

produce the singlet nitrene.^[9] The relaxed S_1 state produces only a minor amount of nitrene when the S_n states are populated initially. This is in agreement with the difference density plot calculations for 2-NpCON₃. The TRIR experiments using 270 and 350 nm radiation confirmed that most of the 2-naphthoylnitrene arises from the S_n ($n \geq 2$) states formed upon 270 nm excitation.^[9]

Optimization of the excited states and calculation of their IR spectra

Recently, using computational methods, we have studied the ground and excited state chemistry of phenyldiazirine and phenyldiazomethane.^[29] The predicted geometric changes upon excitation were in excellent agreement with the results of recent ultrafast experiments.^[29,24,33] Encouraged by these previous studies, we performed geometry optimizations of the S_1 states of $t\text{-BuCON}_3$, PhCON₃, and $p\text{-BpCON}_3$ at the TD-B3LYP/TZVP level of theory; however, because of computational limitations, we were not able to optimize the S_1 excited state of 2-AnCON₃ (Scheme 1). The stationary points obtained on the singlet excited state potential energy surfaces (PES) were confirmed to be

minima by calculating the second derivatives (via a numerical differentiation of the analytical first derivative), and these calculations provided an IR spectral prediction for the S_1 states. The optimized ground and excited state geometries for the aromatic carbonyl azides are shown in Fig. 6.

From the difference density plots (Fig. 4), it is obvious that $p\text{-BpCON}_3$ has a (π,π^*) S_1 state, and the electronic reorganization is delocalized over the entire molecule. Thus, the S_1 geometry of this acyl azide is characterized by changes of the aromatic C=C bond lengths and by only a moderate elongation of the C=O bond. A similar observation was made in the case of 2-NpCON₃ at the same level of theory.^[9] On the other hand, the S_1 state of PhCON₃ is predicted to be an (n,π^*) state localized mainly on the carbonyl unit (Fig. 2). As a result, the C=O bond length is elongated to a greater extent, while only minor changes are predicted for the phenyl unit (Fig. 6).

Although the difference electronic density plot for $t\text{-BuCON}_3$ seems similar to that of the PhCON₃, the S_1 state of $t\text{-BuCON}_3$ has substantial contributions from the azide unit (Fig. 3). As a result, the case of $t\text{-BuCON}_3$ is more complicated; despite several attempts to optimize the geometry of the S_1 state at the

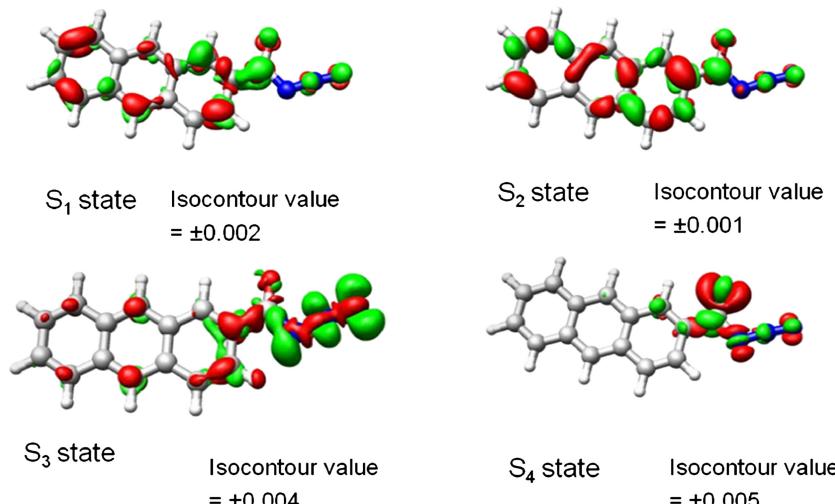


Figure 5. Electron density difference plots for the S_1 to S_4 states of 2-AnCON₃ calculated at the TD-B3LYP/TZVP level of theory. The green contours depict the accumulation of electron density in the excited state, and the red contours illustrate the loss of electron density from the S_0 ground state

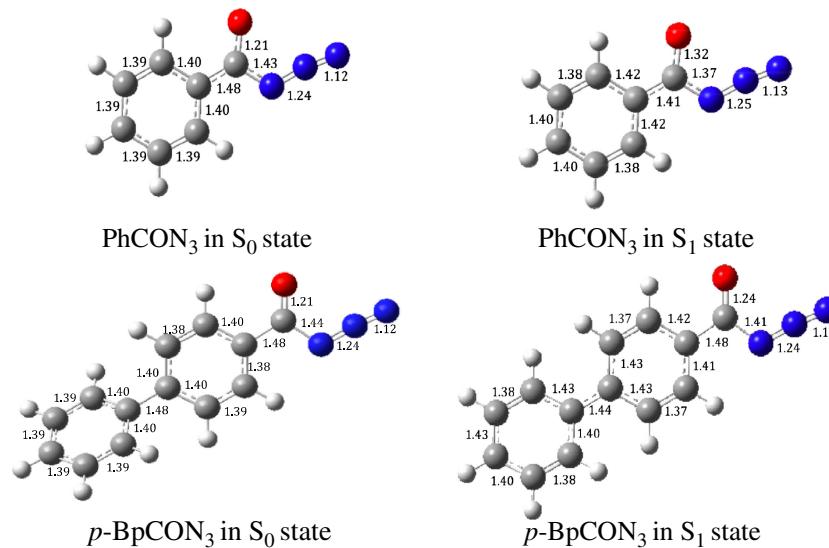


Figure 6. Selected geometrical parameters of the optimized ground (left) and lowest singlet excited (right) states of PhCON₃ (top) and *p*-BpCON₃ (bottom). Bond lengths are shown in Å. The ground and S₁ states were optimized at the B3LYP/TZVP and TD-B3LYP/TZVP levels of theory, respectively

TD-B3LYP/TZVP level, a stationary point could not be located. However, we were able to locate the minimum on the S₁ PES at the TD-B3LYP/SVP level of theory (Fig. 7). To explain a failure to locate a minimum on the S₁ PES at the TD-B3LYP/TZVP level, a comprehensive analysis of the excited state manifold was performed. The section of a ground state PES was computed along the N–N₂ bond. At every step, the ground state geometry was optimized for a specific (OC)N–N₂ bond length, and then vertical excitations to the S₁–S₄ states were calculated to evaluate the energies of the excited state surfaces. We use the term “vertically excited surface” (VES) for these calculated surfaces, and Fig. 8 shows the results of these calculations.

Calculations predict a barrier of about 35–40 kcal/mol (point A) for extrusion of molecular nitrogen on the ground state PES (Fig. 8), and this result is in general agreement with experimental values for similar extrusions.^[34,35] Calculations also predict a very shallow minimum on the S₁ VES (point B). On the other hand, the calculated barrier to extrude molecular nitrogen on the S₁ VES is only about 3 kcal/mol (point C). It should also be noted that both the vertically excited S₁ and S₂ surfaces are very close in energy in the vicinity of point C. These features as well as any slight perturbation by basis set may explain our failure to locate a minimum on the S₁ PES at the TD-B3LYP/TZVP level of theory.

Figure 7 shows that the (OC)N–N₂ bond is significantly elongated and the azide unit is noticeably bent in the optimized structure of the *t*-BuCON₃ S₁ state. As was demonstrated previously,^[30–32] lengthening of the N–N₂ bond and bending of

the azide unit are characteristic features of a *dissociative* state. However, according to the electron density difference plots (Fig. 3), the vertically excited S₂ state is the *dissociative* state. This suggests that during the course of the optimization at the TD-B3LYP/SVP level, the vertically excited S₂ state crossed below that of the vertically excited S₁ state. Thus, energetic and geometric proximity of the (n,π*) S₁ and *dissociative* S₂ states is another reason for the failure to optimize the *t*-BuCON₃ S₁ state at the TD-B3LYP/TZVP level of theory.

As discussed previously, *t*-BuCON₃, PhCON₃, and *p*-BpCON₃ undergo different structural changes upon excitation to their lowest singlet excited states. Nevertheless, all three carbonyl azides in the S₁ state have similar (and intense) vibrational bands for the N₃ stretching mode, and this band is shifted to lower energy as compared with the corresponding bands of the ground state carbonyl azides (Table 2).

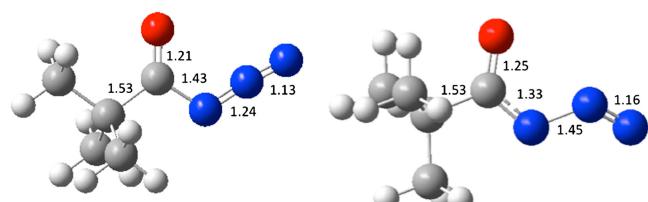


Figure 7. Geometries of the ground (left) and lowest singlet excited (right) states of *t*-BuCON₃ (bond lengths are in Å). The ground and S₁ states were optimized at the B3LYP/SVP and TD-B3LYP/SVP levels of theory, respectively

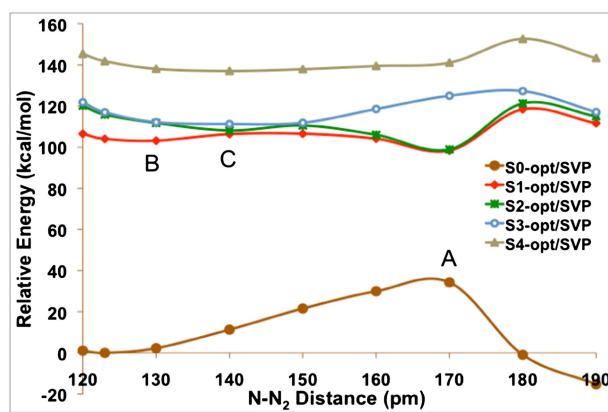


Figure 8. Potential energy surfaces for the ground and first four excited states of *t*-BuCON₃, as calculated at the TD-B3LYP/SVP level of theory. All points on the ground state PES are restricted optimizations with the N–N₂ bond length frozen at the specified value, while all other parameters were allowed to optimize. The vertical excitations to the S₁–S₄ states were then calculated at those ground state geometries to provide an estimate of the “vertically excited surfaces”

Table 2. Unscaled frequencies and intensities of the N_3 stretching modes in the S_0 and S_1 states of acyl azides calculated at the B3LYP/TZVP and TD-B3LYP/TZVP levels of theory, respectively

Acyl azide	S_0		S_1	
	N_3 stretch/ cm^{-1}	Intensity/ $\text{km} \times \text{mol}^{-1}$	N_3 stretch/ cm^{-1}	Intensity/ $\text{km} \times \text{mol}^{-1}$
2-NpCON ₃ ^a	2282	809	2210	2495
PhCON ₃	2283	686	2208	1393
p-BpCON ₃	2282	842	2207	2830
t-BuCON ₃ ^b	2338	574	2125	587

^aFrom Kubicki *et al.*^[9]
^bCalculated at the TD-B3LYP/SVP level.

ULTRAFAST TRIR AND UV-VIS PUMP-PROBE ABSORPTION MEASUREMENTS

In our short communication, results from our initial ultrafast fs TRIR study on the photochemistry of *t*-BuCON₃, PhCON₃, and 2-NpCON₃ (with 270 nm excitation, in chloroform) were reported.^[8] Formation of aryl nitrenes and isocyanates was detected at 1760 and 2265 cm^{-1} , respectively.^[8] Another positive band observed at 2100 cm^{-1} was assigned to the S_1 state of the acyl azides. The latter band decays bi-exponentially (e.g., $\tau_1 = 6.8 \pm 1.3$ and $\tau_2 = 116 \pm 30$ ps for 2-NpCON₃ in chloroform), and the fast component was attributed to the hot S_1 state.^[8,9] The relatively long component was assigned to the thermally relaxed S_1 state of acyl azides.^[8] It was also concluded that deactivation of the S_1 state leads to isocyanate formation.

Recently, we studied the excited state chemistry of 2-NpCON₃ using ultrafast TRIR and UV-vis spectroscopy in a variety of solvents.^[9] In 2-NpCON₃, the 2100 cm^{-1} IR band and a wide transient absorption spectrum in the 350–650 nm UV-vis range were assigned to the S_1 state of 2-NpCON₃, and these assignments were supported by DFT and MS-CASPT2//CASSCF calculations, respectively.^[9] Both the IR and UV-vis absorption bands decayed bi-exponentially in all solvents under study. The time constant of the long-lived component was highly solvent dependent; importantly, polar solvents significantly accelerated the decay of the vibrationally cooled S_1 state of 2-NpCON₃.^[9]

The same approach was applied to study the photochemistry of *t*-BuCON₃, PhCON₃, *p*-BpCON₃, and 2-AnCON₃ in solvents of different polarity (chloroform and acetonitrile). Figure 9 displays the TRIR spectra of PhCON₃ and *t*-BuCON₃^[8] as well as *p*-BpCON₃ and 2-AnCON₃, in chloroform, upon 270 nm excitation (previously published^[8] transient spectra for *t*-BuCON₃, PhCON₃, and for 2-NpCON₃ in chloroform are shown for comparison). The spectral range (2000–2150 cm^{-1}) chosen for study is a region where the strong IR markers of the acyl azides in the S_1 state are predicted. All spectra presented in Fig. 9 were obtained on the same day and with the same experimental conditions (such as pump power, probe intensity, focusing of the pump beam, etc.); moreover, all spectra were normalized to the same intensity of the absorbed 270 nm light. Thus, the spectral changes presented in Fig. 9 involve the same number of excited precursor molecules. Figure 9 demonstrates that all of these acyl azides have a positive IR band at about 2100 cm^{-1} that is present

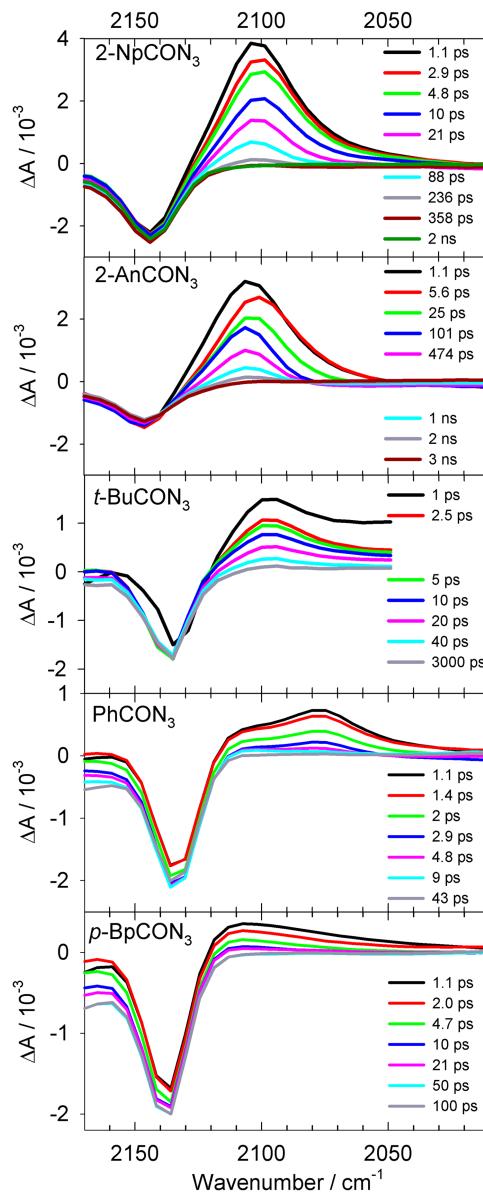


Figure 9. Transient IR spectra produced upon photolysis of *t*-BuCON₃ ($c > 3.5 \times 10^{-3}$ M), PhCON₃ ($c \sim 3.5 \times 10^{-3}$ M), *p*-BpCON₃ ($c \sim 7.2 \times 10^{-4}$ M), and 2-AnCON₃ ($c \sim 2.1 \times 10^{-4}$ M) in chloroform ($\lambda_{\text{exc}} = 270$ nm). Analogous spectra^[9] for 2-NpCON₃ ($c \sim 1.4 \times 10^{-3}$ M) are shown for comparison

immediately after the laser pulse. The position of this band is shifted to lower frequency relative to that of the ground state azide. For all carbonyl azides, the 2100 cm^{-1} band decays bi-exponentially. Consistent with previous work,^[8,9] we assign the short-lived component to the decay of the hot S_1 state, while the longer component is assigned to the relaxed S_1 state. The time constants for both components are presented in Table 3. As discussed earlier, calculations predict that all of these carbonyl azides in the S_1 state have an intense IR band around 2100–2200 cm^{-1} ; thus, calculations support the assignment of the ultrafast TRIR spectra of Fig. 9 to the corresponding lowest singlet excited states of these acyl azides.

As noted earlier, we also performed fs time-resolved UV-vis experiments using 270 nm laser irradiation of these acyl azides. Previously,^[9] a broad transient absorption (350–650 nm) formed within a laser pulse was assigned to the S_1 state of 2-NpCON₃.^[9]

Table 3. Parameters of the bi-exponential decays of the 2100 cm^{-1} band for 2-AnCON₃, 2-NpCON₃, *p*-BpCON₃, PhCON₃, and *t*-BuCON₃ in chloroform ($\lambda_{\text{exc}}=270\text{ nm}$). Time constants obtained by fs UV-vis spectroscopy are also given for comparison

Compound	$A_1/10^{-3}$	$\tau_1/\text{ps}^{\text{a}}$	$A_2/10^{-3}$	$\tau_2/\text{ps}^{\text{b}}$
2-AnCON ₃	1.5 ± 0.1	3.9 ± 0.8	$7.0 \pm 3.0^{\text{c}}$	720 ± 30
2-NpCON ₃	2.7 ± 0.1	$6.8 \pm 1.3^{\text{d}}$	$6 \pm 2^{\text{e}}$	$130 \pm 20^{\text{d}}$
<i>p</i> -BpCON ₃	0.40 ± 0.16	1.0 ± 0.3	0.26 ± 0.06	4.9 ± 0.5
PhCON ₃ ^f	0.47 ± 0.08	$1.6 \pm 0.4^{\text{d}}$	0.20 ± 0.07	$15 \pm 4^{\text{d}}$
<i>t</i> -BuCON ₃ ^f	0.70 ± 0.20	$0.6 \pm 0.2^{\text{d}}$	1.0 ± 0.2	$23 \pm 5^{\text{d}}$

^aHot S_1 .^bThermally relaxed S_1 .^cTime constants obtained by fs UV-vis spectroscopy.^dFrom Kubicki et al.^[8]^eFrom Kubicki et al.^[9]^fNo signal was observed in the 350–650 nm spectral range.

Similar intense and broad transient absorption was also detected upon 270 nm excitation of 2-AnCON₃ in chloroform (Fig. 10a). In contrast to 2-NpCON₃, formation of this transient spectrum is not instantaneous; a rising component with a time constant of about 0.4 ps is necessary to correctly describe the experimental kinetics (Fig. 10b). This fact may be rationalized by taking into account the fact that the S_n state ($n > 3$, Table 1) is pumped with the 270 nm excitation. Thus, the 0.4 ps time constant may be assigned to the lifetime of the upper singlet excited state (probably, S_2). This absorption feature decays bi-exponentially with two different time constants (7.0 ± 3.0 and 900 ± 90 ps), which are in good agreement with the time constants obtained by the ultrafast TRIR method (3.9 ± 0.8 and 720 ± 30 ps, Table 3). The negative signal near 400 nm, visible at long delay times, is due to the ground state depopulation of 2-AnCON₃.

p-BpCON₃ exhibits similar behavior in the ultrafast UV-vis experiments. However, there were no measurable signals in the available spectral range (350–650 nm) upon 270 nm excitation of PhCON₃ and *t*-BuCON₃. The time constants for the S_1 state decay of azides under study measured using both ultrafast techniques are summarized in Table 3.

As mentioned earlier, the decay of the S_1 state of 2-NpCON₃ is accelerated significantly in polar solvents.^[9] To test the generality of this observation, fs TRIR experiments were performed in different solvents for *t*-BuCON₃ and 2-AnCON₃. Indeed, the decay of the S_1 state of *t*-BuCON₃ in acetonitrile was much faster than that in chloroform. However, the decay was mono-exponential because of a very short lifetime in this solvent (3.2 ± 1.0 ps). Because of the absence of an appropriate chromophore, no signals were observed over the 350–650 nm spectral range upon excitation of *t*-BuCON₃ in chloroform and acetonitrile. Upon excitation of 2-AnCON₃ in acetonitrile, the decay of the 2100 cm^{-1} band is bi-exponential with time constants of 5.2 ± 0.3 and 280 ± 30 ps. Similar time constants were obtained with fs UV-vis techniques (5.1 ± 0.5 and 360 ± 90 ps). In chloroform, the decay of the 2100 cm^{-1} band is slower: 3.9 ± 0.8 and 720 ± 30 ps (Table 3). Similar time constants were measured by the fs UV-vis technique (6.5 ± 3.0 and 900 ± 90 ps). These results are consistent with the polarity dependence observed for 2-NpCON₃.^[9]

2-AnCON₃ is a good candidate to test if the S_1 state of acyl azide is the precursor of isocyanate because the lifetime of its S_1 state (720 ± 30 ps in chloroform) is much longer than the typical time constants of vibrational cooling (VC, < 100 ps).^[8,24,36–43]

For 2-NpCON₃, the clear correlation between the decay of the S_1 state and isocyanate formation was observed only when the relatively long-lived S_1 state was directly pumped using 350 nm excitation.^[9] As the contribution of the hot S_1 state decay is pronounced upon 270 nm excitation, the formation of isocyanate should be biphasic.^[9] Figure 11 presents the formation of the isocyanate band upon excitation of 2-AnCON₃ in chloroform. Just after a laser pulse, hot isocyanate is formed, and its spectrum undergoes a shift to higher energies within 100 ps. During

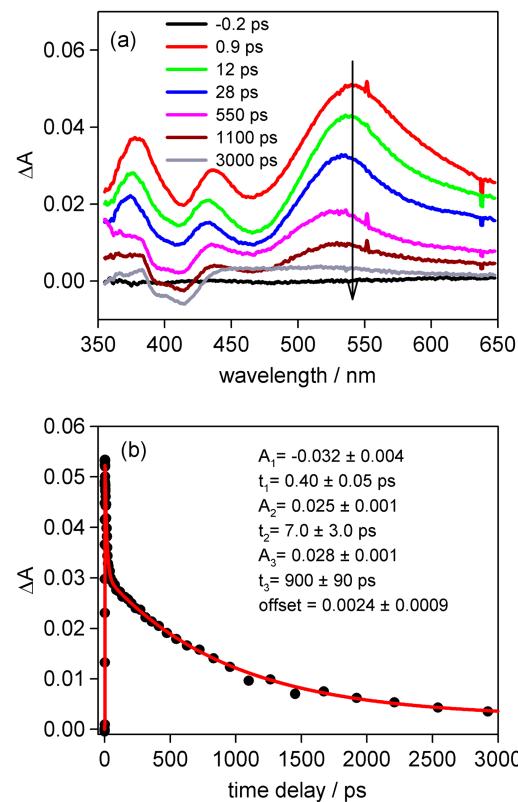


Figure 10. (a) The transient absorption UV-vis spectra recorded at different time delays after excitation ($\lambda_{\text{exc}}=270\text{ nm}$, $c \sim 2.1 \times 10^{-4}\text{ M}$) of 2-AnCON₃ in chloroform at ambient temperature. (b) The transient absorption kinetics was recorded at 530 nm and is best fit by three-exponential function. The first time constant is that of S_n ($n > 1$) state, while the second and third time constants correspond to hot and relaxed S_1 states, respectively

this time, slow formation of the isocyanate from the relaxed S_1 state should also proceed. After about 100 ps, the maximum of the isocyanate band does not change, and a slow growth of the isocyanate band is clearly visible. The time constant of this growth (670 ± 110 ps, Fig. 11b) is consistent with the time constant of the S_1 decay (720 ± 30 ps). This is additional, direct experimental evidence that both the hot and relaxed S_1 states of acyl azides are the precursors of the resulting isocyanate product.

A little different behavior was observed for *p*-BpCON₃, which has a hot and relaxed S_1 state with a very short lifetime (~1 and ~5 ps respectively, Table 3). In this case, the isocyanate product is formed faster than the rate of VC (Fig. 12). Therefore, the apparent growth up to 100 ps, monitored at about 2272 cm⁻¹, is due to VC (Fig. 12b). After about 100 ps, no spectral changes are observed (Fig. 12a). In this case, the integration of the area under the spectral envelope may give a better approximation of the rate constant of isocyanate formation. However, the experiment does not cover the whole spectral range of the isocyanate band, and additionally, the intensity for higher vibrational levels should be scaled.^[44] The appropriate scaling could not be performed as the position of vibrational levels is not known and signals from different vibrational levels overlap. Figure 12(c) demonstrates that the integrated signal is almost constant after 10–20 ps. This is consistent with the fact that the S_1 state of *p*-BpCON₃, which has a lifetime of 5 ps, is a precursor of isocyanate.

Formation of the singlet nitrene *p*-BpCON was also monitored using fs TRIR spectroscopy (Fig. 13). The nitrene band with maximum at about 1720 cm⁻¹ is formed within the laser pulse and then shifts to higher energy over 100 ps, a pattern which is typical of VC.

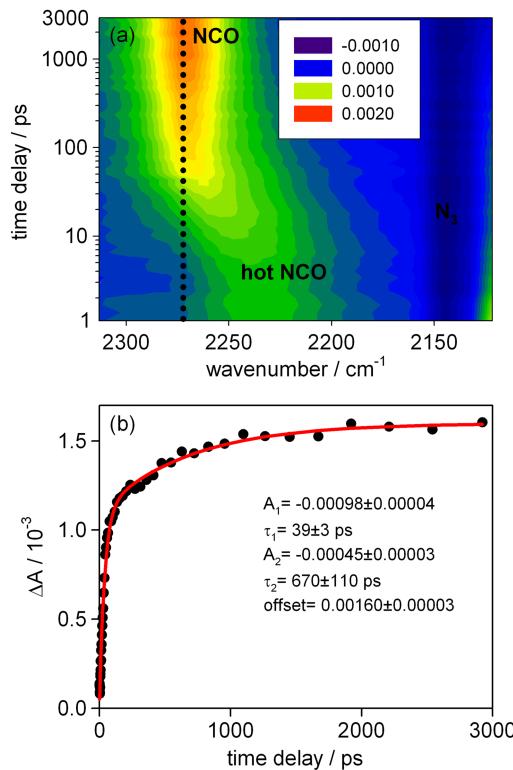


Figure 11. Isocyanate formation upon 270 nm excitation of 2-AnCON₃ in chloroform ($c \sim 2.1 \times 10^{-4}$ M). (a) 2D contour plot of TRIR spectra. Note that the time delay is given in logarithmic scale. (b) The kinetics of isocyanate formation recorded at 2270 cm⁻¹ (dotted line on the upper 2D contour plot)

As VC is much slower than the expected time constant of nitrene formation (~5 ps) and the amplitude of nitrene band is very low, it is impossible to obtain experimental evidence that the S_1 state (in addition to the S_n states) is a precursor of the nitrene. Similar results were obtained for 2-AnCON₃. Thus, the fs TRIR technique does not provide an opportunity to prove that the S_1 state is a precursor of nitrene when the upper S_n ($n > 1$) states are pumped or when the S_1 lifetime is shorter than typical VC processes observed in solvent as applied in these experiments.

As reported previously,^[8,9] the recovery of the ground state was not observed by fs TRIR spectroscopy for all acyl azides. The negative signal due to the bleaching of the precursor does not change its amplitude up to 3 ns time delay (Figs. 12b and 13b).

Although the aforementioned spectroscopic data are in agreement with theory, one question remains to be answered, specifically why the lifetimes of the S_1 states of 2-AnCON₃ and 2-NpCON₃ are considerably longer than the corresponding S_1

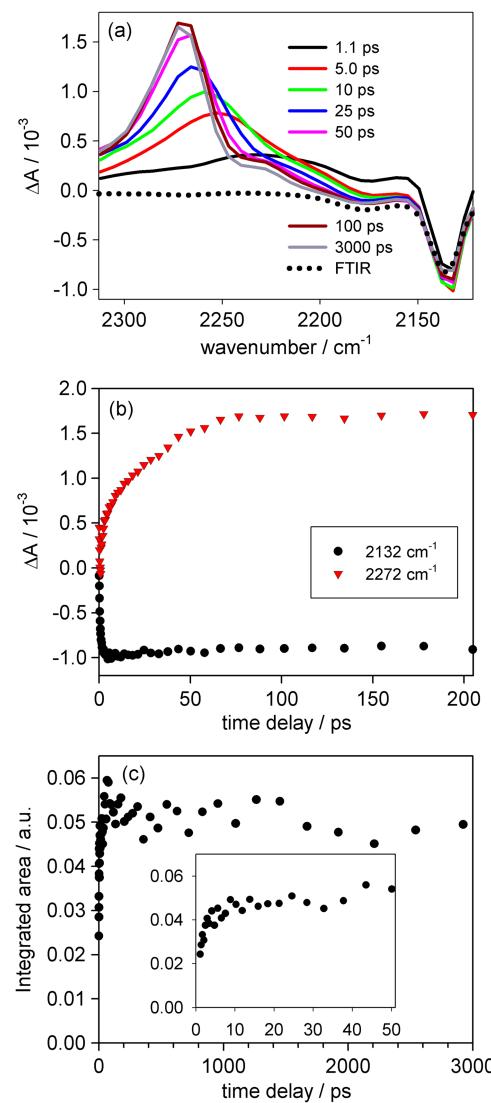


Figure 12. Isocyanate formation upon 270 nm excitation of *p*-BpCON₃ in chloroform ($c \sim 7.2 \times 10^{-4}$ M). (a) TRIR spectra at selected time delays. (b) Kinetics of the isocyanate formation recorded at 2270 cm⁻¹ and of the ground state bleaching at 2132 cm⁻¹. (c) Integrated signal of the isocyanate band (plot a) versus time delay (inset presents only the 0–50 ps time range)

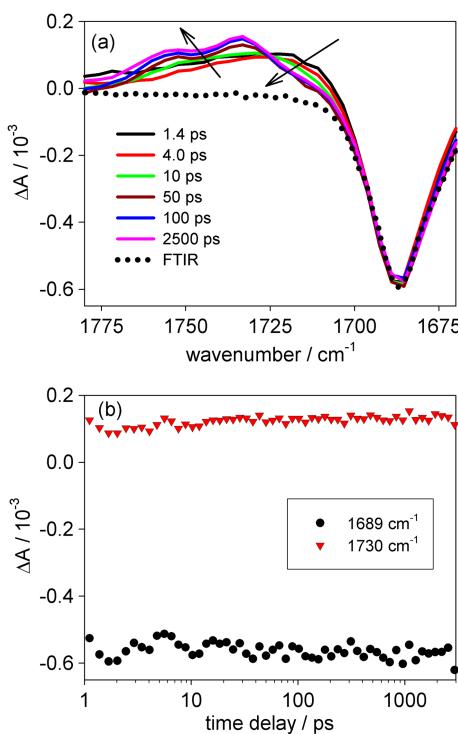


Figure 13. (a) The TRIR spectra produced upon photolysis of *p*-BpCON₃ ($\lambda_{\text{exc}} = 270 \text{ nm}$, $c \sim 7.2 \times 10^{-4} \text{ M}$) in chloroform are given at selected time delays. The normalized steady state IR absorption spectrum of *p*-BpCON₃ is shown as a dotted line. (b) The kinetics recorded at 1730 cm⁻¹ (nitrene absorption band) and at 1689 cm⁻¹ (bleaching of the ground state, C=O vibration mode)

state of *p*-BpCON₃, PhCON₃, and *t*-BuCON₃. A possible origin of this difference is that the long(er)-lived S_1 states of 2-AnCON₃ (720 ps) and 2-NpCON₃ (120 ps) are (π,π^*) in character, while the other carbonyl azides in this study have (n,π^*) S_1 states (<25 ps). This suggestion is in general agreement with our calculations, however, with the exception of *p*-BpCON₃, where the predicted S_1 state of *p*-BpCON₃ is localized on the entire molecule instead of having pure (n,π^*) character. The energy difference (~3 kcal/mol) between the S_1 state and the (n,π^*) state (S_2) is within the error bar of the theoretical calculations. Thus, a simple explanation is that the S_1 state of *p*-BpCON₃ is actually (n,π^*) in nature.

A second question is why the S_1 state decay for *p*-BpCON₃ is faster than that of the S_1 states of PhCON₃ and *t*-BuCON₃. We speculate that this might be due to dihedral angle rotation around the biphenyl ring's C-C bond in the S_1 state of *p*-BpCON₃, perhaps via some rapid energy relaxation mechanism, and one which is not available for PhCON₃ and *t*-BuCON₃. To test this hypothesis, experiments on fluorenyl carbonyl azide are ongoing.

CONCLUSIONS

The photochemistry of a series of carbonyl azides (PhCON₃, *p*-BpCON₃, 2-AnCON₃ and *t*-BuCON₃) was studied using ultrafast time-resolved IR and UV-vis spectroscopy in two solvents of different polarity (chloroform and acetonitrile). The experimental findings were supported and explained using DFT calculations. Quantum chemical calculations of the electronic density distribution in both the ground and Frank-Condon excited states yielded difference density plots, and the re-distribution of the

electron density in the excited states was useful for predicting the nature, geometries, and lifetimes of these excited states. The lowest singlet excited states (S_1 states) of both *t*-BuCON₃ and PhCON₃ were found to be (n,π^*) in nature, while *p*-BpCON₃ and 2-AnCON₃ have the S_1 state of (π,π^*) type. Although the S_1 states of these carbonyl azides are different, either (n,π^*) or (π,π^*) , they were predicted to have similar vibrational bands for the N₃ stretching mode at around 2100–2200 cm⁻¹. This result can be attributed to the similar geometry of the azide unit in the S_1 state of the carbonyl azides.

Indeed, for all acyl azides under study, a positive band at about 2100 cm⁻¹, assigned to the S_1 state, was detected upon 270 ns excitation in chloroform and acetonitrile. A broad transient absorption in the range of 350–650 nm was assigned to the S_1 state. As in the case of 2-NpCON₃,^[8,9] the S_1 states of the acyl azides studied here decay bi-exponentially. This is due to the decay of both the hot and vibrationally cooled S_1 states. It was also demonstrated that, similar to the case of 2-NpCON₃,^[9] a polar solvent (acetonitrile) accelerates the decay of the relaxed S_1 state of *t*-BuCON₃ and 2-AnCON₃.

In agreement with previous results,^[8,9] the data obtained for 2-AnCON₃ clearly confirm that the S_1 state of an acyl azide is the precursor of the isocyanate product even when the S_n state ($n \geq 2$) is initially populated. However, attempts to monitor nitrene formation were complicated by the low amplitude of nitrene band and slow VC. Therefore, we were unable to obtain direct experimental evidence that the S_1 state is the precursor of nitrene. However, the results of this work are consistent with earlier findings that the S_n state of an acyl azide produces nitrene with higher efficiency than the S_1 state.^[8,9] Additionally, the hot S_1 state may produce nitrene faster and with higher efficiency than the thermalized S_1 state. The shift of a nitrene band to higher energy on the 100 ps time scale clearly shows that nitrene is formed in a vibrationally excited (hot) state.

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