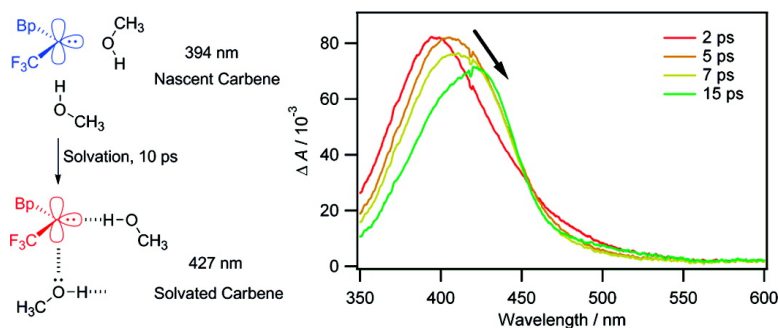Article

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The Dynamics of Carbene Solvation: An Ultrafast Study of *p*-Biphenylyltrifluoromethylcarbene

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Abstract: Ultrafast photolysis (λ_{ex} = 308 nm) of *p*-biphenylyltrifluoromethyl diazomethane (BpCN$_2$CF$_3$) releases singlet *p*-biphenylyltrifluoromethylcarbene (BpCCF$_3$) which absorbs strongly at 385 nm in cyclohexane, immediately after the 300 fs laser pulse. The initial absorption maximum shifts to longer wavelengths in coordinating solvents (nitrile, ether, and alcohol). In low viscosity coordinating solvents, the initial absorption maximum further red shifts between 2 and 10 ps after the laser pulse. Similar effects are observed upon ultrafast photolysis of 2-fluorenyltrifluoromethyl diazomethane (FlCN$_2$CF$_3$) and therefore cannot be associated with torsional motion around the two phenyl rings of the biphenyl compound. Instead, the effect is attributed to the dynamics of solvation of the singlet carbene. The time constant of solvation in normal alcohols lengthens with solvent viscosity in a linear manner. Furthermore, the time constants of the red shift in methanol-*O*-d (16 ps), ethanol-*O*-d (26 ps), 2-propanol-OD (40 ps), and 2,2,2-trifluoroethanol-*O*-d (14 ps) are longer than those recorded in methanol (9.6 ps, KIE = 1.7), ethanol (14.3 ps, KIE = 1.8), 2-propanol (28 ps, KIE = 1.4), and 2,2,2-trifluoroethanol (4.4 ps, KIE = 3.2), which indicates that the solvent reorganization involves formation of hydrogen bonds. The kinetic data are consistent with motion of the solvent to achieve a specific interaction with the carbene, with the creation of a new hydrogen bond. The solvated carbene reacts with the solvent over tens, hundreds, and thousands of ps, depending upon the solvent.

I. Introduction

A closed shell singlet carbene contains a filled hybrid orbital and an empty p-π orbital. This has encouraged organic chemists to think of singlet carbenes as zwitterionic intermediates.[1] Singlet carbenes are electron-deficient reactive intermediates which react rapidly with nucleophiles.[1] For example, singlet carbenes react with ethers, nitriles, and ketones to form ylides. Mechanistic carbene chemists have long wondered if carbenes may enjoy specific solvation with a coordinating solvent *prior* to reaction with the solvent to form ylides or other products. Given the fact that a putative carbene-solvent complex will rapidly collapse to form a more stable ylide, garnering experimental or computational evidence of carbene solvation is quite a challenge. Indeed, many calculations predict that solvent−carbene complexes collapse to form product in a barrierless process.[2−4]

Experimental evidence of carbene solvation has been reported. Tomioka and co-workers reported that 1,4-dioxane has a dramatic effect on the O−H insertion selectivity of phenylcar-bene.[5] Khan and Goodman determined the dissociation energy of the methylene-benzene complex to be 8.7 ± 3.1 kcal/mol, using picosecond optical grating calorimetry.[6] This experimental value was consistent with the predictions of their *ab initio* calculations.[6] Moss, Yan, and Krogh-Jespersen discovered the modulation of alkylhalocarbene reactivity by π-complexation to aromatics.[7] Ruck and Jones reported solvent effects on the ratio of 1,1-dimethylcyclopropane to 2-methyl-2-butene products formed upon isomerization of *t*-butylcarbene,[8] presumably as a result of solvation.

It has been proposed that alkenes interact with singlet carbenes, prior to product formation, by the formation of a complex between the π bond of the alkene and the empty p-orbital of the singlet carbene. Reversibly formed complexes of this nature were proposed to explain the observation of negative enthalpies of activation in the reaction of halophenyl carbenes with alkenes.[9,10] Other explanations of this effect have also been proposed.[2−4]

As mentioned previously, it is well-known that alkyl carbenes undergo numerous rearrangements to form a spectrum of

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products. When diazo or diazirine compounds are employed as photochemical precursors, plots of the ratio of the carbene intermolecular reaction product with carbene trap to its intramolecular rearrangement product versus the concentration of the carbene trap, is curved. To explain this phenomenon, Liu et al. proposed the formation of carbene–alkene complexes, and that these complexes form intramolecular rearrangement products at a rate that is competitive with collapse of the carbene–alkene complex to form cyclopropane.[11] Later experimental work favored a different interpretation, the rearrangement in the excited states (RIES) of diazo or diazirine precursors.[12−14]

Tippmann et al. reported that a small amount of 1,4-dioxane in Freon-113 can dramatically extend the lifetime of carbonylcarbenes, which exist on microsecond timescales.[15] This work utilized the pyridine ylide method, a technique which does not observe the carbene directly. Nevertheless, using this method, they showed that a small amount of dioxane in Freon-113 depresses the rate constant of reaction of carbene with alkene. The authors proposed that solvation of the carbene modulated its absolute reactivity much like a protic solvent can depress the reactivity of a nucleophile by a specific solvent–solute interaction, in this case hydrogen bonding. Tippmann et al. found that TRIR spectroscopy could easily distinguish carbonylcarbene from carbene–ylide but could not distinguish free carbonylcarbene from ether solvated carbonylcarbene. However, it was clear from TRIR spectroscopy that the presence of ether depressed the reactivity of the carbene toward alkene as the conversion of carbene to carbene–ether ylide is relatively slow.[15]

Moss and co-workers have recently reported that the HOMO–LUMO, $\sigma \rightarrow p$, absorption of methylchlorocarbene can be observed at 544 nm in pentane using nanosecond time-resolved laser flash photolysis techniques.[16] The carbene absorption maxima is also found at 544 nm in benzene, tetrahydrofuran (THF), and 1,4-dioxane. In anisole and 1,3-dimethoxybenzene (DMB), the absorption maximum is found at 520 and 512 nm, respectively. The arylether-solvated carbene absorption maxima are blue-shifted relative to those in pentane, benzene, THF, and 1,4-dioxane. Over hundreds of nanoseconds, the arylether solvated carbenes react to form new species which absorb at 368 nm (anisole) and 375 nm (DMB). On the basis of computational work, these bands were assigned to charge-transfer transitions of methylchlorocarbene–arylether complexes.

Using ultrafast time-resolved techniques, we herein report direct evidence that two singlet carbenes, *p*-biphenylyltrifluoromethylcarbene (BpCCF$_3$) and its 2-fluorenyl analogue (FlCCF$_3$), enjoy specific solvation in tetrahydrofuran (THF), acetonitrile, and methanol and that the process of solvation requires 2–10 ps. This is the first measurement of the solvation time of a carbene. In alcohol solvents of greater viscosity, tens to hundreds of ps is required for solvent reorganization. Kinetic isotope

effects in alcohol solvents will reveal that part of the solvent reorganization involves the formation of a new hydrogen bond. Solvent–carbene complexes react over tens, hundreds, or thousands of ps to form reaction products depending on the solvent.

II. Results and Discussion

**II.1. Non-Polar Solvents. II.1.1. Cyclohexane and Cyclohexene.** There are many scales that attempt to measure solvent polarity. Eisenthal and co-workers[17−19] discovered that singlet to triplet diphenylcarbene (DPC) intersystem crossing (ISC) time constants correlate with the Dimroth $E_T(30)$ parameters of several solvents.[20] The fastest rates of ISC were observed in solvents with small $E_T(30)$ values. Hence, we will follow the Eisenthal group and use the Dimroth scale to classify solvent polarity in this study.

Ultrafast photolysis ($\lambda_{ex} = 308$ nm) of *p*-biphenylyltrifluoromethyl diazomethane (BpCN$_2$CF$_3$) produces the transient spectra shown in Figure 1. A broad transient absorption, centered at 510 nm, is formed and decays within the instrument response time (300 fs) and is attributed to an excited singlet state of the diazo compound (^{1}BpCN$_2$CF$_3$*). The decay of ^{1}BpCN$_2$CF$_3$* is accompanied by the growth of transient absorption attributed to singlet carbene ^{1}BpCCF$_3$ (see Scheme 1) at 385 nm (Table 1). This is in good agreement with the results of TDDFT calculations[21,22] (Supporting Information (SI), Table S1), which predict a vertical transition at 362 nm ($f = 0.5497$). The absorption maximum of ^{1}BpCCF$_3$ does not shift in cyclohexane on the ps time scale (Table 1) but the absorption band does sharpen (Figure 1b). The sharpening of this band over 10 ps is attributed to vibrational cooling (VC).[14,23−27] The decay of the carbene is monoexponential ($\tau = 200 \pm 10$ ps, Figure 2a).

The photochemistry of diazo compound BpCN$_2$CF$_3$ was also studied in cyclohexane-d_{12}. The carbene lifetime is 300 ± 30 ps in the deuterated solvent (Table 1 and Figure 2b). This result indicates that the lifetime of ^{1}BpCCF$_3$ in cyclohexane is controlled, in part, by the reaction of ^{1}BpCCF$_3$ with solvent by C–H insertion. This is in sharp contrast with biphenylcarbene analogues ^{1}BpCH and ^{1}BpCCH$_3$, where the singlet carbenes cleanly relax to their lower energy triplet states in cyclohexane prior to reaction with this solvent.[14,28] Theoretical analyses of singlet carbene intermolecular C–H insertion reactions indicate that the empty p-orbital of the carbene initially coordinates with

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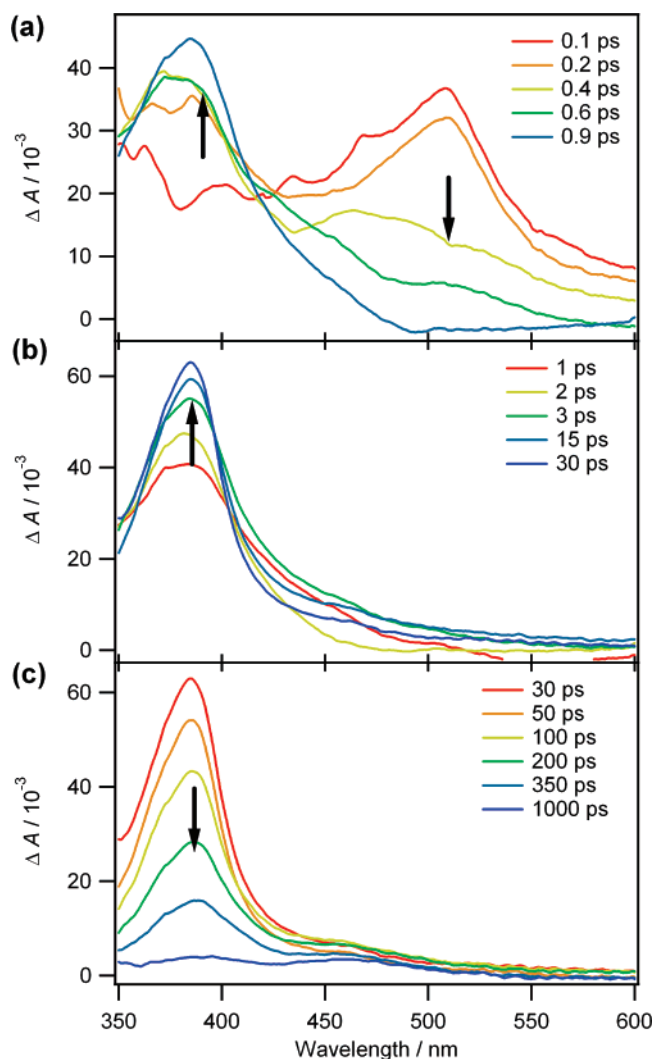
Figure 1. Transient spectra produced by ultrafast photolysis of *p*-biphenylyltrifluoromethyl diazomethane in cyclohexane. The spectra were generated by ultrafast LFP (308 nm) with time windows of (a) 0.1−0.9 ps, (b) 1−30 ps, and (c) 30−1000 ps.

the electron pair of the C−H bond.[29−31] Thus, the highly electron withdrawing CF_3 group increases the electrophilicity of this carbene compared to biphenylyl and biphenylylmethyl carbenes and boosts the rate of bimolecular C−H insertion reactions of $BpCCF_3$. This observation is consistent with a previously reported product study of tolyltrifluoromethylcarbene which concluded that almost all the photoproducts formed in cyclohexane originate from the singlet carbene.[32] Vibrational cooling of $^1BpCCF_3$ proceeds at the same rate in cyclohexane and cyclohexane-d_{12} (Table 1).

BpCH   **BpCCH$_3$**
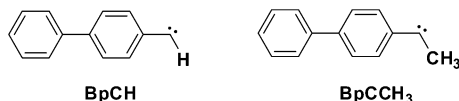
DFT calculations predict that the triplet state of carbene $^3BpCCF_3$ is 4.18 kcal/mol lower in Gibbs free energy than the

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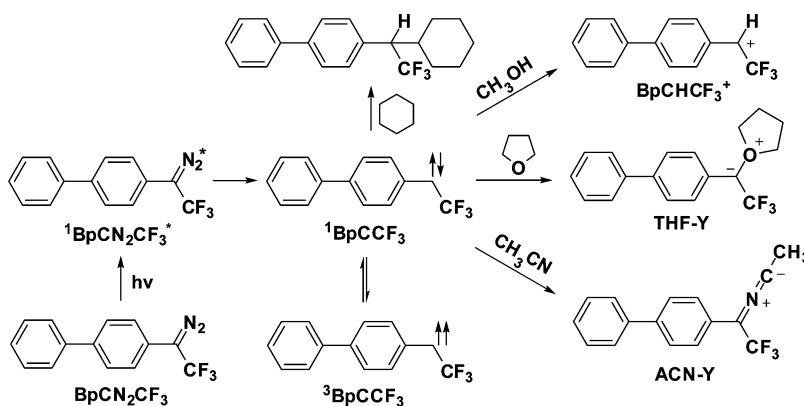(32) Platz, M.; Admasu, A. S.; Kwiatkowski, S.; Crocker, P. J.; Imai, N.; Watt, D. S. *Bioconjugate Chem.* **1991**, *2*, 337−341.

lowest, closed shell, singlet state in the gas phase at 298 K (Table 2). In cyclohexane, the triplet is also predicted to be the ground state. Our results are consistent with the work of Hadad and Toscano which demonstrated that polar solvents preferentially stabilize singlet carbenes, relative to triplet carbenes.[33] This is fully consistent with the expected zwitterionic nature of the singlet carbene and the biradical nature of the triplet carbene.

The decay of singlet carbene $^1BpCCF_3$ is not accompanied by the growth of transient absorption which can be attributed to a triplet carbene spin isomer. This is not surprising as TDDFT calculations predict that the triplet carbene will absorb at 332 nm (SI, Table S2), outside the detection window of our ultrafast spectrometer. However, time-resolved studies of the photochemistry of $BpCN_2CF_3$ were performed on a nanosecond spectrometer which allows detection at shorter wavelengths. Nanosecond laser flash photolysis of $BpCN_2CF_3$ in cyclohexane produced transient absorption centered at 325 nm with a lifetime of 6 μs in argon purged solution (SI, Figures S1 and S2a). The lifetime of the carrier of this transient absorption shortens to 1.1 μs and 275 ns in air and oxygen saturated solutions, respectively (SI, Figures S2b and S2c). The carrier of 325 nm absorption is assigned to $BpCCF_3$ in its triplet ground state on the basis of the TDDFT calculations (SI, Table S2) and its oxygen sensitivity. Thus, we conclude that $^1BpCCF_3$ decays by both intersystem crossing (ISC) and by insertion into solvent C−H bonds in cyclohexane.

The lifetime of $^1BpCCF_3$ in cyclohexene is shortened to 110 ± 4 ps (Table 1 and Figure 2c). We posit simply that $^1BpCCF_3$ reacts more rapidly with a carbon−carbon double bond than with a carbon−hydrogen bond to form the expected cylcopropane product.

The transient spectra of $^1BpCCF_3$ are identical in cyclohexane and in cyclohexene. If a carbene−alkene complex is formed it must have the same spectrum as the "free" carbene. We do not believe that a carbene−alkene complex is present in this system but cannot eliminate this possibility.

II.1.2. Aromatic and Halogenated Solvents. Ultrafast time-resolved studies were performed in benzene, fluorobenzene, chlorobenzene, hexafluorobenzene, dichloromethane, and chloroform (SI, Figures S3−S8). In benzene, the initial carbene absorption maximum is observed at 400 nm, a 15 nm red shift relative to cyclohexane. The initial absorption maximum red shifts to 407 nm with a time constant of 6 ps (Table 1). In halogenated solvents, the initial absorption maxima again are red-shifted relative to cyclohexane. In halogenated solvents, the initial absorption maxima shifts further to the red by more than 10 nm over 3−7 ps (Table 1).

The lifetimes of $^1BpCCF_3$ are unusually long in benzene, and the halogenated benzenes and methanes of this study. A similar halogenated solvent effect was observed in our previous studies of fluorenylidene.[34] In that work we proposed that the empty orbital of singlet fluorenylidene complexed with nonbonding electrons of the halogenated solvent. As singlet and triplet fluorenylidene will interact differently with the solvent we proposed a Franck−Condon like factor on the ISC process which led to a slower ISC rate. We will present our analysis of the ground state multiplicity of $BpCCF_3$ as a function of solvent

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Scheme 1

Table 1. Lifetimes and Spectral λ_{max} Shift of Carbene ^{1}BpCCF$_3$ and Solvent Properties

solvent	τ_{BpCCF3} (ps)	$\lambda_{max}^{initial}$ (nm)	λ_{max}^{final} (nm)	$\tau_{\text{VC/red shift}}$ (ps)	η^e (mPa·s)	$E_T(30)^h$ (kcal·mol^{-1})
cyclohexane	200 ± 10	385	385	7.7 ± 2.2^d	0.894	30.9
cyclohexane-d_{12}	300 ± 30	385	385	7.5 ± 1.8^d		
cyclohexene	110 ± 4	390	390	1.4 ± 0.3^d	0.625	32.2
benzene	800 ± 40	400	407	6.1 ± 1.6	0.604	34.3
fluorobenzene	860 ± 60	392	403	7.0 ± 2.2	0.550	37.0
chlorobenzene	NR^a	399	412	3.2 ± 0.3	0.753	36.8
hexafluorobenzene	NR^a	385	397	3.3 ± 0.4	2.79	34.2
dichloromethane	NR^a	396	407	3.0 ± 0.7	0.413	40.7
chloroform	NR^a	393	408	3.0 ± 0.3	0.537	39.1
acetonitrile	580 ± 60	400	410	0.4 ± 0.1	0.369	45.6
tetrahydrofuran	90 ± 10	396	401	1.3 ± 0.2	0.456	37.4
1,4-dioxane	79 ± 5	393	399	0.6 ± 0.2	1.177	36.0
diisopropyl ether	450 ± 20	390	390	15 ± 6^d	0.313^f	34.1
methanol	31 ± 4	394	427	9.6 ± 0.5	0.544	55.4
ethanol	90 ± 10	386	421	14.3 ± 0.6	1.074	51.9
1-propanol	250 ± 40	388	427	45 ± 3	1.945	50.7
1-butanol	270 ± 40	388	425	59 ± 4	2.54	49.7
1-pentanol	360 ± 30	391	425	73 ± 2	3.62	49.1
1-hexanol	400 ± 30	385	426	100 ± 5	4.58	48.8
1-octanol	570 ± 40	385	427	172 ± 9	7.29	48.1
2-propanol	380 ± 10	388	425	28 ± 2	2.04	48.4
2,2,2-trifluoroethanol	13 ± 1^b	385	420^c	4.4 ± 0.7	1.768^g	59.8
methanol-O-d	49 ± 5	390	425	16 ± 2		
ethanol-O-d	210 ± 43	382	420	26 ± 1		
2-propanol-O-d	450 ± 57	383	423	40 ± 2		
2,2,2-trifluoroethanol-O-d	30 ± 2^b	382	423	14 ± 1		

^{a} The lifetime is too long to be resolved on the spectrometer. ^{b} The lifetime is determined by the growth of the carbenium ion since the shift of the carbene band is too dramatic (cf. Figure 6). ^{c} The final λ_{max} cannot be determined accurately since the carbene band is severely obscured by the carbenium ion band (cf. Figure 6). ^{d} Since in these solvents, there is no spectral shift and $\tau_{\text{red shift}}$ is not applicable. These values are the growth time constants at spectral λ_{max}. ^{e} The viscosity data (25 °C) are obtained from CRC Handbook of Chemistry and Physics, 87th edition, unless otherwise specified. ^{f} The viscosity data (25 °C) are obtained from *J. Chem. Eng. Data*, **2006**, *51*, 261. ^{g} The viscosity data (25 °C) are obtained from *J. Phys. Chem.*, **1958**, *62*, 1311. ^{h} All the $E_T(30)$ data are obtained from *Chem. Rev.*, **1994**, *94*, 2319.

and the solvent dependence of the ISC rates in a subsequent article. We believe that the explanation previously proposed for fluorenylidene will also explain the BpCCF$_3$ data.

II.2. Polar Solvents (Solvents Containing either a Nitrogen or an Oxygen Atom). II.2.1. Acetonitrile (ACN). Ultrafast photolysis of the diazo compound BpCN$_2$CF$_3$ in acetonitrile (ACN) produces the transient spectrum shown in Figure 3. Once again, the spectrum of the excited state, ^{1}BpCN$_2$CF$_3$*, is formed and decays within the instrument response function (300 fs). Transient absorption assigned to ^{1}BpCCF$_3$ grows as the diazo excited state decays. In ACN, the initial absorption maximum of the carbene is seen at 400 nm, as compared to its value of 385 nm in nonpolar solvents. Between 1 and 6 ps after the laser pulse, the initial absorption maximum grows and shifts from 400 to 410 nm,[35] and the shape of the absorption band narrows at the same time.

The carbene decay is clearly biexponential ($A_1 = 0.031$, $\tau_1 = 18 ± 5$ ps and $A_2 = 0.076$, $\tau_2 = 580 ± 60$ ps, Figure 4). Note that the carbene decay was monoexponential in cyclohexane. The fast component (18 ps) is assigned to VC of ^{1}BpCCF$_3$, based on narrowing of the absorption band. Under similar conditions using acetonitrile as solvent, the decay of ^{1}BpCCH$_3$ was also biexponential,[14] whereas the decay of ^{1}BpCH was monoexponential.[28]

Two explanations of this effect were proposed.[14] We speculated that the enhanced VC process in ^{1}BpCCH$_3$ relative to ^{1}BpCH might be a result of 1,2 migration of hydrogen or could be due to the rotational motion of the methyl group. As a C−F bond is stronger than a C−H bond, and is therefore less likely

(35) The majority of the spectra shift happens from 1 to 2 ps. After 2 ps, the spectra show mainly growth of the intensity rather than spectra shift.
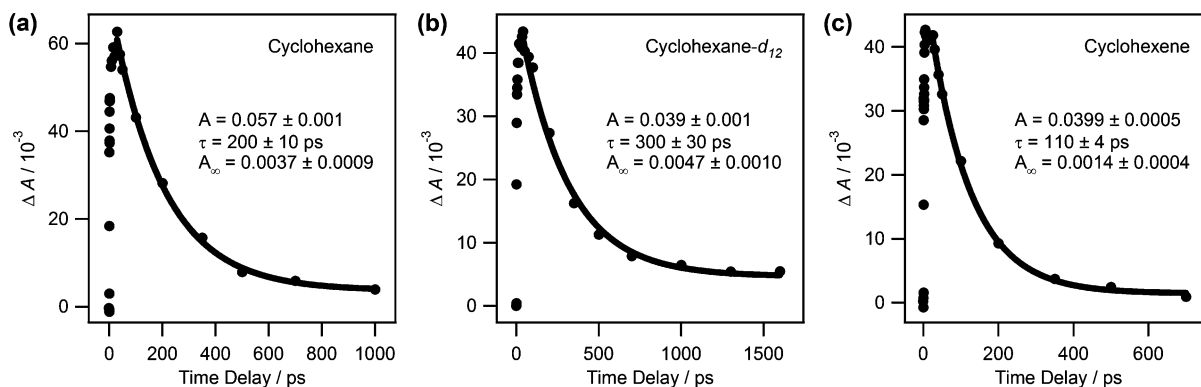
Figure 2. The kinetic traces were produced by ultrafast photolysis (λ_{ex} = 308 nm) of *p*-biphenylyltrifluoromethyl diazomethane in (a) cyclohexane (λ_{pr} = 385 nm), (b) cyclohexane-d_{12} (λ_{pr} = 385 nm), and (c) cyclohexene (λ_{pr} = 390 nm).

Table 2. The Calculated Singlet−Triplet Gaps (kcal·mol^{-1}) for *p*-Biphenylyltrifluoromethylcarbene (BpCCF$_3$), *p*-Biphenylylcarbene (BpCH), and *p*-Biphenylylmethylcarbene (BpCCH$_3$) in the Gas Phase and Solvents Using the Theory of B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)[a]

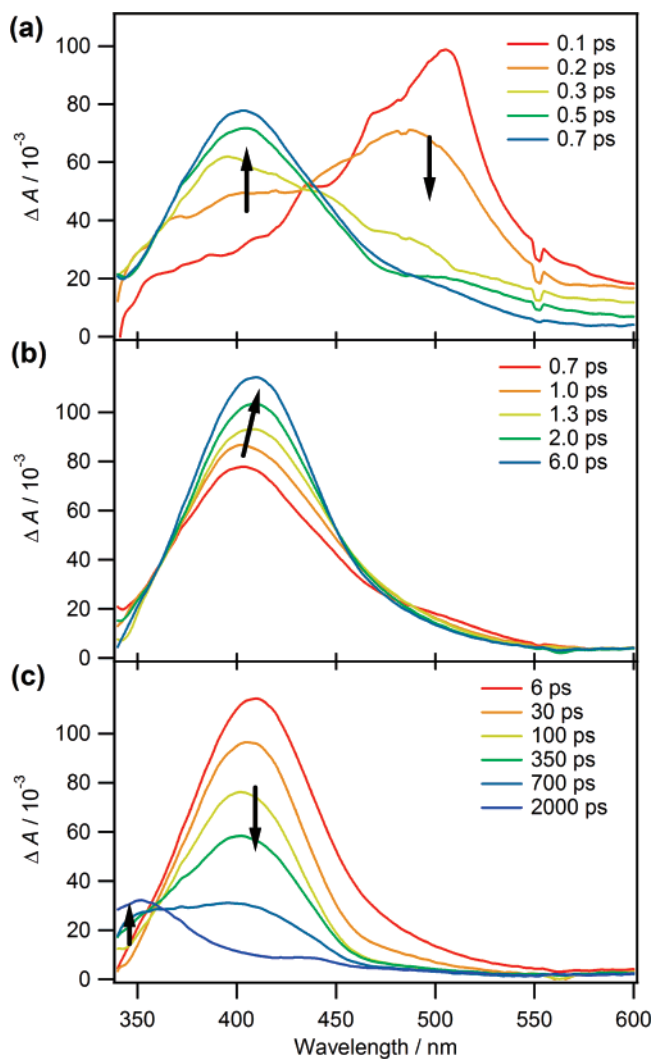|	BpCCF$_3$			BpCH	BpCCH$_3$
	gas phase	cyclohexane[b]	acetonitrile[b]	gas phase	gas phase
ΔE_{ST} (0 K)	3.04	1.06	−2.13	4.78	5.10
ΔH_{ST} (298 K)	3.37	1.42	−1.74	5.04	5.10
ΔG_{ST} (298 K)	4.18	2.32	−0.91	5.61	6.76

[a] The energy is calculated at the B3LYP/6-311+G(d,p) level of theory using the B3LYP/6-31G(d) geometry and scaled zero-point vibrational energy (scaling factor 0.9806) and thermal and entropic corrections as appropriate. A positive value of the singlet−triplet energy gap indicates that the triplet state is more stable. [b] Using the PCM implicit solvation model. The results are uncorrected.[46]

to migrate, and as VC is still observed, we conclude that the biexponential decay and efficient VC is due to rotation of the methyl and trifluoromethyl group.

The decay of ^{1}BpCCF$_3$ leads to the formation of transient absorption at 350 nm. The carrier of this absorption is assigned to carbene−acetonitrile ylide ACN-Y. The observed absorption maximum of ACN-Y is in excellent agreement with the results of TDDFT calculations (λ_{max} = 351 nm, *f* = 0.3859, SI, Table S3). The time constants of carbene decay and ylide growth are the same, within experimental error as required by the spectral assignments. The lifetime of ^{1}BpCCF$_3$ in acetonitrile is much longer than that in cyclohexane. This behavior is typical and was discovered first by the Eisenthal group with diphenylcarbene[17,19] and later by Schuster and co-workers with fluorenylidene[36] and finally in our studies of ^{1}BpCH[28] and ^{1}BpCCH$_3$[14].

ACN-Y
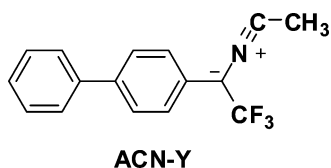
DFT calculations (Table 2) predict that BpCCF$_3$ has a triplet ground state in cyclohexane but has a singlet ground state in acetonitrile. We do not observe the formation of a triplet carbene in this system, instead the carbene reacts with ACN to form a nitrile ylide. Thus, it is possible that the long lifetime of
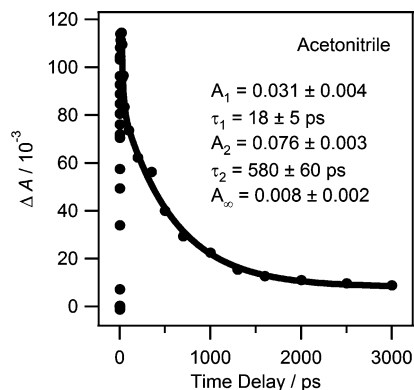
(36) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833−6845.

Figure 3. Transient spectra produced by ultrafast photolysis of *p*-biphenylyltrifluoromethyl diazomethane in acetonitrile. The spectra were generated by ultrafast LFP (308 nm) with time windows of (a) 0.1−0.7 ps, (b) 0.7−6.0 ps, and (c) 6−2000 ps.

^{1}BpCCF$_3$ in ACN is a result of the carbene having a singlet ground state in this solvent and a lifetime that is no longer controlled, even in part, by ISC to a lower energy triplet spin isomer.

We previously mentioned that the decay of ^{1}BpCCF$_3$ could be well fit to an exponential function in cyclohexane. On the

Figure 4. The kinetic trace was produced by ultrafast photolysis ($\lambda_{ex} = 308$ nm) of *p*-biphenylyltrifluoromethyl diazomethane in acetonitrile and probed at 410 nm.

basis of the previous studies for singlet diphenylcarbene[37] and singlet *p*-biphenylylmethylcarbene,[14] we propose that vibrational cooling is faster in cyclohexane than in acetonitrile. In cyclohexane, the vibrational cooling of ^{1}BpCCF$_3$ is manifest as a growth and sharpening of the absorption band with a time constant of 7.7 ps. In acetonitrile, the initial growth of ^{1}BpCCF$_3$ may show the influence of carbene vibrational cooling. However, in acetonitrile the majority of the vibrational cooling is expressed as a decay process transpiring 10−40 ps after the laser pulse. Thus, the decay of ^{1}BpCCF$_3$ is monoexponential in cyclohexane, but is biexponential in acetonitrile.

II.2.2. Tetrahydrofuran (THF), 1,4-Dioxane, and Diisopropyl Ether. The data obtained in THF resemble that in ACN (SI, Figure S9). Carbene absorption is observed initially centered at 396 nm and then it shifts to 401 nm over 7 ps.

The lifetime of ^{1}BpCCF$_3$ is 90 ± 10 ps in THF (Table 1). The decay of the carbene is accompanied by the growth of transient absorption at 360 nm (SI, Figure S9b). The carrier of this spectrum is assigned to ylide THF-Y. The assignment of the 360 nm transient absorption to ylide THF-Y is in good agreement with TDDFT calculations which predict transient absorption at 343 nm ($f = 0.4138$, SI, Table S4). In 1,4-dioxane, the results are essentially the same as those recorded in THF. Both ps red shifts in the carbene absorption maxima and the formation of ylide dioxane-Y are observed (SI, Figure S10). The lifetime of ^{1}BpCCF$_3$ is 75 ± 5 ps in 1,4-dioxane (Table 1), which is the same as that in THF within experimental error.

THF-Y   Dioxane-Y
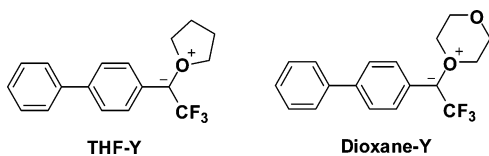
The experiment was repeated in diisopropyl ether which is more sterically encumbered than is THF. In this solvent, the initial carbene absorption was observed at 390 nm (SI, Figure S11). The transient absorption at the absorption maximum continues to grow 1−50 ps after the laser flash owing to vibrational cooling but unlike the results obtained in THF and 1,4-dioxane, the value of λ_{max} remains unchanged. The lifetime of the singlet carbene in diisopropyl ether is 450 ± 20 ps. We do not observe the growth of an ylide as the carbene decays in
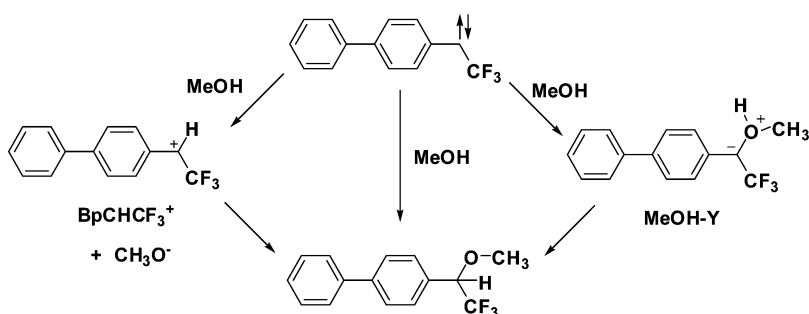
(37) Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428−6438.
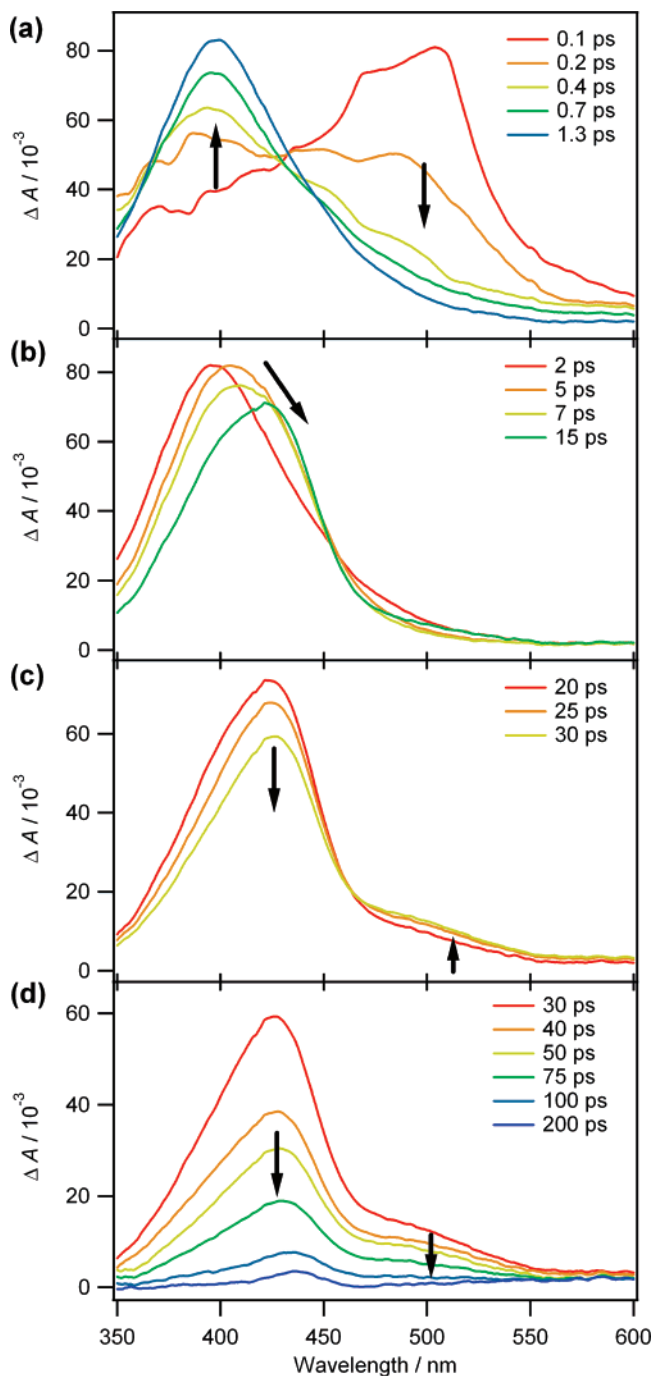
Figure 5. Transient spectra produced by ultrafast photolysis of *p*-biphenylyltrifluoromethyl diazomethane in methanol. The spectra were generated by ultrafast LFP (308 nm) with time windows of (a) 0.1−1.3 ps, (b) 2−15 ps, (c) 20−30 ps, and (d) 30−200 ps.

diisopropyl ether. We will posit that steric bulk prevents a specific solute−solvent interaction and subsequent ylide formation in diisopropyl ether.

II.2.3. Methanol. The transient spectra produced by ultrafast photolysis of BpCN$_2$CF$_3$ in methanol are shown in Figure 5. As before, the transient spectrum of ^{1}BpCN$_2$CF$_3$* decays and is replaced by that of ^{1}BpCCF$_3$ which originally has its maximum at 394 nm. The initial absorption maximum shifts to 427 nm with a time constant of 10 ps. The red shift is also observed in methanol-OD but proceeds more slowly (KIE = 1.6). Similar results were observed in ethanol and 2-propanol but in these solvents the evolution of the secondary red shift

Scheme 2

proceeds over a longer time period. The time constants of the red shift in methanol-OD (16 ps), ethanol-OD (26 ps), and 2-propanol-OD (40 ps) are longer than those recorded in methanol (9.6 ps, KIE = 1.7), ethanol (14.3 ps, KIE = 1.8), and 2-propanol (28 ps, KIE = 1.4).

Singlet carbenes react with alcohols by at least three mechanisms to eventually form ethers (Scheme 2).[38,39] The carbene can act as a base and abstract a proton from methanol to form a benzylic cation–alkoxide ion pair which will subsequently collapse to form the observed ether product. The carbene can also directly insert into an OH bond in a concerted process resembling the direct insertion of a singlet carbene into a C–H bond. Alternatively, the empty p-orbital of the carbene can react with a nonbonding pair of electrons of the oxygen atom of the alcohol to form an ylide which subsequently undergoes a proton shift to form the ylide product.

When an aryl carbene abstracts a proton from an alcohol it forms a benzylic cation which is UV–vis active. The benzhydryl cation has been observed following reaction of singlet diphenylcarbene with methanol or water. As the molar absorptivity of benzhydryl cation is known, Kohler et al. were able to deduce that proton transfer accounts for 30% of the total reactivity of single diphenylcarbene with methanol in neat methanol.[37]

Chemists have often used isotope effects to understand the mechanism of reaction of singlet carbenes with alcohols. The lifetime of [1]BpCCF$_3$ in methanol is 31 ± 4 ps. In CH$_3$OD, the carbene lifetime is extended to 49 ± 5 ps. This demonstrates that singlet carbene BpCCF$_3$ reacts, in part, by either abstraction of a proton to form cation BpCHCF$_3^+$ and/or by direct insertion into the O–H bond of the alcohol. As singlet biphenylcarbene [1]BpCH decays in methanol, a strong transient absorption signal of *p*-phenylbenzyl cation grows and then decays. There is not a corresponding strong growth of transient absorption accompanying the decay of [1]BpCCF$_3$, but the weak transient absorption growing in the 500 nm region might be due to that of the formed cation in very low yield. This conjecture is strengthened upon repeating the experiment in 2,2,2-trifluoro-ethanol (TFE). In the more acidic solvent, the formation of a transient absorption centered at 475 nm is greatly enhanced and is assigned to the cation (Figure 6). Thus, we conclude that in methanol proton transfer is a very minor component of the reaction of [1]BpCCF$_3$ with the solvent and that the observed kinetic isotope effect on the carbene lifetime must be due to concerted O–H bond insertion. Proton transfer with [1]BpCCF$_3$ is only important in the presence of a strongly acidic solvent

such as TFE because of the electron-withdrawing, cation destabilizing nature of the CF$_3$ group. Also, it is interesting to note that the time constant of red shift is in TFE-OD (14 ps) is also longer than that recorded in TFE (4.4 ps, KIE = 3.2).
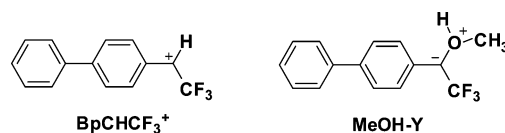
There is no spectroscopic evidence to support the formation of a carbene–alcohol ylide (MeOH-Y), which intuition suggests should have an absorption spectrum similar to that of ether ylide THF-Y. To our knowledge this type of ylide has never been observed. It is possible that ylide MeOH-Y isomerizes in femtoseconds to form the corresponding ether by subsequent intra- or intermolecular proton shift, which renders the concentration of MeOH-Y too low to be detected. DFT calculations (SI, Table S5) predict that the methanol ylide is a species with a finite lifetime in the gas phase and TDDFT calculations predict it will have an absorption maximum of 317 nm ($f = 0.5417$), 26 nm to the blue of the predicted absorption maximum of the THF-ylide. It is interesting to note that calculations predict that the OH group of methanol forms a hydrogen bond with the CF$_3$ group and that the three C–F bonds in the CF$_3$ group are nonequivalent.

[1]BpCCF$_3$ has a longer lifetime in methanol than does diphenylcarbene,[37] *p*-biphenylcarbene,[28] or *p*-biphenylmethyl-carbene.[14] This is not surprising because singlet carbenes react with alcohols by three mechanisms and the electron-withdrawing trifluoromethyl group destabilizes adjacent cationic centers and decelerates the proton-transfer component of the reaction.

II.3. 2-Fluorenyltrifluoromethylcarbene (FlCCF$_3$). To learn if the ps growths and red shifts observed in this study are related to torsional motions in the biphenyl group, as observed in other species containing biphenyl moieties,[40–42] a rigid analogue, 2-fluorenyltrifluoromethyldiazomethane (FlCN$_2$CF$_3$) was synthesized. Ultrafast photolysis of FlCN$_2$CF$_3$ in acetonitrile produces transient absorption attributed to an excited-state of the diazo compound (500 nm) and singlet 2-fluorenyltrifluoromethylcarbene ([1]FlCCF$_3$) with initial absorbance at 427 nm. Vibrational cooling is observed (2–30 ps) and the absorption maximum shifts from 427 to 432 nm (SI, Figure S12a). Even more dramatic results are realized in methanol. In alcohol

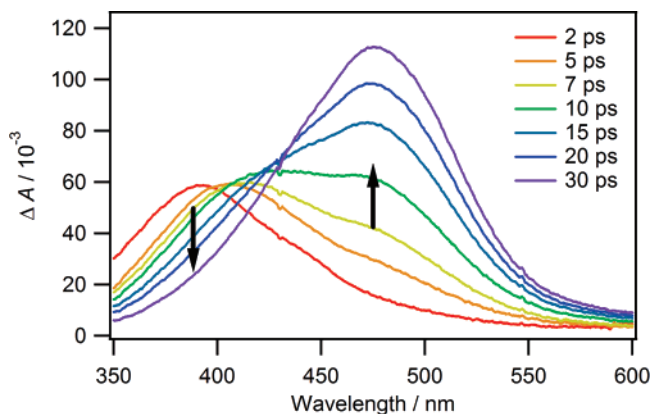(38) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc., Perkin Trans. 2* **1971**, 23−31.
(39) Bethell, D.; Newall, A. R.; Stevens, G.; Whittaker, D. *J. Chem. Soc., Perkin Trans. 2* **1969**, 749−754.

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(41) Leonard, J. D., Jr.; Gustafson, T. L. *J. Phys. Chem. A* **2001**, *105*, 1724−1730.
(42) Tan, X.; Gustafson, T. L.; Lefumeux, C.; Burdzinski, G.; Buntinx, G.; Poizat, O. *J. Phys. Chem. A* **2002**, *106*, 3593−3598.

Figure 6. Transient spectrum produced by ultrafast photolysis of *p*-biphenylyltrifluoromethyl diazomethane in 2,2,2-trifluoroethanol. The spectrum was generated by ultrafast LFP (308 nm) with a time window of 2−30 ps.

solvent the initial transient absorbance of the singlet carbene shifts from 415 to 435 nm between 2 and 20 ps after the laser flash (SI, Figure S12b). In cyclohexane the initial FlCCF$_3$ carbene absorption maximum is at 405 nm and does not shift between 2 and 20 ps after the flash (SI, Figure S12c). Removing the torsional freedom of motion of the two phenyl rings by their incorporation into a rigid fluorenyl ring system does not eliminate the multi-ps shift in absorption maxima observed with BpCCF$_3$ in polar solvents. Thus, motion along the torsional coordinate does not account for the observed red shift. Another effect must be responsible for this observation.
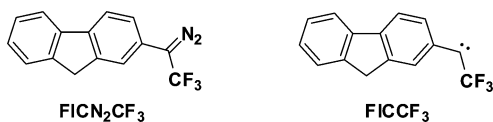

II.4. Studies of a Homologous Series of Alcohols. The photochemistry of BpCN$_2$CF$_3$ was investigated by ultrafast time-resolved techniques in the series of normal alcohols from methanol to *n*-octanol. In every case, the excited-state of the diazo compound is observed and its decay is accompanied by the growth of the singlet carbene. The absorption maximum of the singlet carbene undergoes a red shift in each alcohol.

Over this series the acidity of the solvent, the polarity of the solvent and the viscosity of the solvent vary in a regular manner (Table 1). As shown in Figure 7, the time constant of the red shift correlates linearly with the viscosity of the solvent. This demonstrates that the red shift is associated with motion and reorganization of the solvent. The magnitude of the red shift is roughly correlated with empirical parameters for solvent polarity $E_T(30)$ (SI, Figure S13).

III. Discussion: Carbene Solvation Dynamics

The most remarkable observation in this work is that the initial transient absorption attributed to singlet *p*-biphenylyltrifluoromethylcarbene BpCCF$_3$ varies with solvent polarity and then undergoes a further red shift in acetonitrile, tetrahydrofuran, and methanol. In low viscosity solvents, this shift proceeds 2−10 ps after the ultrafast laser pulse. The same pattern is observed with trifluoromethylfluorenyl-diazomethane, thus the red shift cannot be due to torsional motions involving the two phenyl
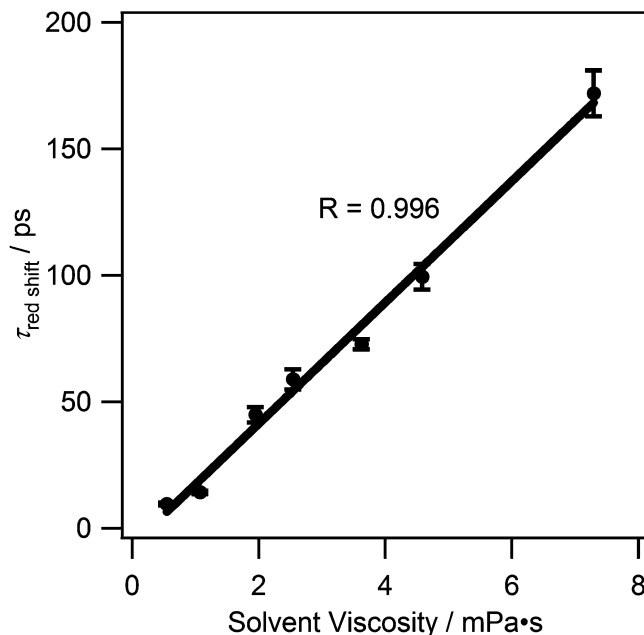
Figure 7. A plot of singlet *p*-biphenylyltrifluoromethylcarbene (^{1}BpCCF$_3$) red shift time constants ($\tau_{red\ shift}$) versus solvent viscosities.

rings. Although a red shift is observed in THF, this effect is not present in a sterically encumbered ether, diisopropyl ether. The time constant of solvation in normal alcohols lengthens with solvent viscosity in a linear manner. Furthermore, the time constants of the red shift in methanol-*O*-d (16 ps), ethanol-*O*-d (26 ps), 2-propanol-*O*-d (40 ps), and 2,2,2-trifluoroethanol-*O*-d (14 ps) are longer than those recorded in methanol (9.6 ps, KIE = 1.7), ethanol (14.3 ps, KIE = 1.8), 2-propanol (28 ps, KIE = 1.4), and 2,2,2-trifluoroethanol (4.4 ps, KIE = 3.2). The data are consistent with motion of the solvent to achieve a specific interaction with the carbene, the creation of a new hydrogen bond. The solvated carbene reacts with the solvent over tens, hundreds, and thousands of ps, depending upon the solvent.

Moss and co-workers[16] found that the absorption maxima of methylchlorocarbene in pentane measured 50 ns after the laser flash is at 544 nm. Presumably, this is the absorption maxima of the optimally solvated carbene in this solvent. The solvated carbene absorption maxima are the same in pentane, benzene, THF, and 1,4-dioxane. In the case of methylchlorocarbene and arylethers, a blue shift of the absorption maxima was observed in contrast to this study where a red shift is consistently observed. We posit that this difference is related to the fact that in methylchlorocarbene, a $\sigma \rightarrow$ p transition is monitored, whereas in ^{1}BpCCF$_3$ we observe a $\pi \rightarrow \pi^*$ transition (SI, Figure S14). The Moss group finds that both π and ylidic complexes were observed with both methylchlorocarbene and benzylchlorocarbene. We have not studied arylether solvents but find that ^{1}BpCCF$_3$-THF and 1,4-dioxane solvated carbenes collapse to form ylides.

Singlet carbene BpCCF$_3$ will have a closed-shell structure with a filled and an empty nonbonding orbital on the carbene carbon. The principal carbene of this study, singlet BpCCF$_3$ is particularly electron deficient because of the trifluoromethyl substituent. This will increase the strength of the interaction of its empty p-orbital with the nonbonding electrons of a coordinating solvent. In acetonitrile and THF only the empty p orbital on the carbene center will profit from solvation and we propose

that the fully solvated carbene has a red-shifted absorption maximum relative to the nascent singlet carbene. This argument is bolstered by the fact that there is no secondary red shift observed in a sterically encumbered ether, diisopropyl ether, where the interaction between the empty p-orbital and non-bonding electrons of the ether is sterically blocked.

Alcohol solvents can interact with both the filled and empty nonbonding orbitals on the carbene carbon. Hence, the red shift is more dramatic in alcohols. The oxygen atom of the alcohol will interact with the empty orbital and the acidic alcohol proton (of the same or yet another alcohol molecule) can coordinate with the filled in-plane nonbonding orbital of the carbene. This explains why the solvent shifts are so dramatic in alcohol solvents. It explains why there is an O−H/O−D isotope effect on the dynamics of the red shift as the process is associated with the formation of a new hydrogen bond. (Note that methanol can hydrogen bond to fluorine atoms of the CF_3 group in both the diazo precursor and the carbene, these are not shown as they are not expected to reorganize upon nitrogen extrusion.)

394 nm   427 nm
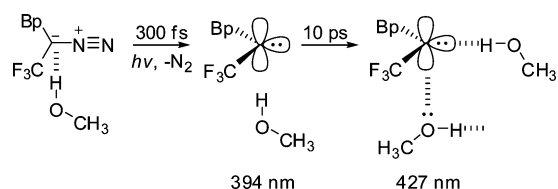
We posit that solvent reorganization does not transpire during the 300 fs lifetime of the diazo excited state. Solvent reorganization must require multiple picoseconds to allow hydrogen bonding to the nonbonding pair of electrons on the carbene center. It seems intuitive that the rate of this reorganization will slow as the solvent viscosity increases and will have a dependence on isotopic composition (O−H versus O−D). There is precedent for this interpretation. In fact, it is well-known that the time constant of solvation depends on the viscosity of the solvent.[43] The solvation time constants of the excited-state of Coumarin 113 in different normal alcohols have been determined, ranging from tens to hundreds of picoseconds as determined by shifts in fluorescence maxima.[44]

IV. Experimental

Calculations. DFT and TDDFT calculations were performed using the Gaussian 03 suite of programs[45] at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory with single point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The electronic spectra were computed using time-dependent density functional theory of Gaussian 03 at the B3LYP/6-311+G(d,p) level and 20 allowed electronic transitions were calculated.

Ultrafast Spectroscopy. Ultrafast UV−vis broadband absorption measurements were performed using the home-built spectrometer

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described previously.[27] Samples were prepared in 50 mL of solvent with absorption 1.0 at the excitation wavelength with 1.0 mm optical length.

Materials. All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade and used as received.

The Preparation of Trifluoromethylketones. 2.66 g of anhydrous aluminum chloride (20 mmol) was mixed with 50 mL of dichloromethane. The suspension was cooled in an ice bath to 0 °C. Then, 4.20 g of trifluoroacetic acid anhydride was dissolved in 15 mL of dichloromethane and added to the suspension slowly. The solution was stirred for 15 min. Then, 1.54 g of biphenyl in 10 mL of dichloromethane was added dropwise over 30 min. The reaction mixture was bright yellow at the beginning of the addition and finally turned brown. After the addition of the biphenyl solution, the reaction mixture was stirred for 1 h at room temperature. The completion of the reaction was confirmed by GC−MS. The reaction mixture was poured into a mixture of 50 mL of concentrated HCl, 150 mL of water, and 150 g of ice with vigorous stirring. The organic phase was separated and the water phase was washed with 30 mL of dichloromethane three times. The organic layer was then washed by $NaHCO_3$ and saturated NaCl solutions and dried over $NaSO_4$. The solvent was removed leaving slightly yellow product. The product can be recrystalized from hexanes and colorless crystal was afforded (1.08 g, 70%). 4-Biphenylyl trifluoromethyl ketone, ^1H NMR (500 MHz, TMS, $CDCl_3$): δ 8.16 (d, J = 8.0 Hz, 2H), 7.79−7.76 (m, 2H), 7.66−7.64 (m, 2H), 7.52−7.49 (m, 2H), 7.47−7.44 (m, 1H). ^{13}C NMR (125 MHz, TMS, $CDCl_3$): δ 180.1 (q, J_{C-F} = 35.0 Hz) 148.2, 139.1, 130.8 (q, J_{C-F} = 2.0 Hz), 129.1, 128.9, 128.6, 127.6, 127.4, 116.8 (q, J_{C-F} = 291.3 Hz). ^{19}F NMR (376 MHz, $PhCF_3$, $CDCl_3$): δ −72.3 (s). 2-Fluorenyl trifluoromethyl ketone was prepared following the same procedure (75% of yield). 2-Fluorenyl trifluoromethyl ketone, ^1H NMR (500 MHz, TMS, $CDCl_3$): δ 8.24 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.92−7.88 (m, 2H), 7.63−7.61 (m, 1H), 7.47−7.42 (m, 2H), 4.00 (s, 2H). ^{13}C NMR (125 MHz, TMS, $CDCl_3$): δ 180.2 (q, J_{C-F} = 34.6 Hz), 148.9, 144.9, 143.5, 139.8, 129.6, 128.9, 128.0, 127.3, 126.6, 125.3, 121.4, 120.1, 116.9 (q, J_{C-F} = 291.4 Hz), 36.8. ^{19}F NMR (376 MHz, $PhCF_3$, $CDCl_3$): δ −71.8 (s).

The Preparation of the Diazo Compounds. A 10 mmol sample of the trifluoroketone and a 10 mmol sample of tosylhydrazine were dissolved in 30 mL of anhydrous THF. The solution was refluxed for 30 min. The solvent was removed leaving the tosylhydrazone. The tosylhydrazone was dried overnight under vacuum to remove trace amount of water. Then the tosylhydrazone was dissolved in 50 mL of anhydrous THF and 10 mL of 1.0 M sodium methoxide methanol solution was added slowly. The solution was allowed to stir for 2 h. The solvent was then removed with a rotary evaporator. The solid tosylhydrazone salt was broken up with a spatula and transferred to another 50 mL flask. A 20 mL portion of ethylene glycol was added to the flask and the mixture was slowly heated to 80 °C with stirring. The solution was kept at 80 °C for 5−10 min until the orange color no longer darkened. Then the mixture was cooled to room temperature, and 15 mL of pentane was added with continued stirring. The organic extract was removed by pipet and the procedure was repeated a total of five times. The combined organic extracts were washed with 30 mL of 5% sodium hydroxide solution, with a saturated sodium chloride solution, and dried over sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give *p*-biphenylyltrifluoromethyl diazomethane as an orange solid (∼30% of yield). 4-Bp-CN_2−CF_3, ^1H NMR (500 MHz, TMS, DMSO-d_6): δ 7.79 (d, J = 8.0 Hz, 2 H), 7.68 (d, J = 7.5 Hz, 2 H), 7.48 (t, J = 8.0 Hz, 2 H), 7.38 (t, J = 7.5 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, $PhCF_3$, $CDCl_3$): δ −57.3 (s). FT-IR (neat) 2045 cm^{-1}. The same procedure was used to prepare 2-Fl-CN_2-CF_3 (∼20% of yield). 2-Fl-CN_2-CF_3, ^1H NMR (500 MHz, TMS,

CDCl$_3$): δ 8.24 (s, 1 H), 8.13 (d, $J = 8.1$ Hz, 1 H), 7.90 (m, 2 H), 7.62 (m, 1 H), 7.45 (m, 2 H), 4.00 (s, 2 H). ^{19}F NMR (376 MHz, PhCF$_3$, CDCl$_3$): δ −57.2 (s). FT-IR (neat) 2055 cm^{-1}.

V. Conclusions

Ultrafast photolysis of *p*-biphenyltrifluoromethyl diazomethane BpCN$_2$CF$_3$ releases singlet *p*-biphenyltrifluoromethylcarbene ^{1}BpCCF$_3$ within 300 fs of the laser pulse. The initial absorbance of the carbene is solvent dependent and is red-shifted in coordinating solvents. Transient absorption attributed to the singlet carbene continues to grow 2−10 ps after the laser pulse in many non-coordinating solvents due to vibrational cooling. In coordinating solvents, the growth in transient absorption is accompanied by a further red shift. The growth in transient absorption and the secondary red shift are attributed to the dynamics of solvation of the singlet carbene.

Supporting Information Available: Complete ref 45; TDDFT calculations in Table S1−S5, nanosecond and ultrafast LFP spectra, kinetic traces, and molecular orbitals in Figure S1−S14. This material is available free of charge via the Internet at http://pubs.acs.org.

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