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Computational and Experimental Studies of the Effect of Substituents on the Singlet−Triplet Energy Gap in Phenyl(carbomethoxy)carbene

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The effect of aromatic substitution on the singlet−triplet energy gap in substituted phenyl(carbomethoxy)carbene (X−Ph−C−CO_2CH_3, **PCC**) has been explored by time-resolved infrared (TRIR) spectroscopy and gas-phase computational methods. The ground state of para-substituted **PCC** is calculated to change from the triplet state in *p*-NO_2-**PCC** ($\Delta G_{ST} = 6.1$ kcal/mol) to the singlet state in *p*-NH_2-**PCC** ($\Delta G_{ST} = -2.8$ kcal/mol). The absence of solvent perturbation in the TRIR spectra of *p*-$N(CH_3)_2$-**PCC** (which should have electronic properties similar to *p*-NH_2-**PCC**) and parent **PCC** is consistent with their ground states lying $>\pm 2$ kcal/mol from the next available electronic state, in line with the computational results. The observation of solvent perturbation in the TRIR spectra of *p*-OCH_3-**PCC** and *p*-CH_3-**PCC** implies that their ground states lie $<\pm 1$ kcal/mol from their next available electronic state. This is in agreement with our computational results, which predict a gas-phase ΔG_{ST} of -0.8 and 1.6 kcal/mol for *p*-OCH_3-**PCC** and *p*-CH_3-**PCC** as compared to ΔG_{ST} values of -3.9 and -1.3 kcal/mol from polarizable continuum model (PCM) calculations with acetonitrile as a solvent. Gas-phase computational results for the meta- and ortho-substituted **PCC** species are also presented, along with selected linear free energy (LFE) relationships for the para and meta species.

Introduction

Much of the interest in the chemistry of α-diazocarbonyl compounds has involved the propensity for ketene formation (Wolff rearrangement).[1] This process is important in a diverse range of synthetic applications,[2] where its uses include, inter alia, inducing ring-contraction processes and one-carbon homologation of carboxylic acids in the Arndt−Eistert sequence. For biological processes, the Wolff rearrangement in α-diazo ketones has been used to effect, photochemically, the cleavage of DNA.[3] The Wolff rearrangement is also used in the preparation of polymers with microlithographic applications in positive photoresists.[4]

In the light of these important applications, a detailed understanding of carbonyl−carbene reactivity is of interest not only for the advancement of basic science but also for the continued development of these applied technologies. There remain, however, several factors that complicate our understanding of these reaction mechanisms. First, there is the ever-present question of whether the reactivity observed is indeed that of the free carbene or of an excited state of the precursor,[5] a carbene−olefin complex,[6] an unstable precursor isomer,[7] or an excited state of the carbene.[8] Even if this issue can be settled, the reactivity of the free carbene is still not easily determined unless one knows its preferred spin state.[9] Therefore, it is vitally important to understand the electronic configuration of the carbene under scrutiny. However, even if one were to know the relative energies of the electronic states of a carbene (singlet and triplet),

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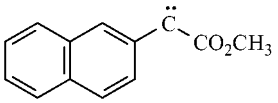
chemistry often arises from the more reactive singlet state, regardless of which is the lowest energy electronic state. The two most commonly invoked mechanisms accounting for this reactivity are those by Bethell and co-workers[10] and Griller, Nazran, and Scaiano.[11]

Thus, before one can begin to understand the reactivity of a given carbene, one must know the relative energy difference between the lowest singlet and triplet electronic states. A recent series of papers has examined this issue in the case of 2-naphthyl(carbomethoxy)carbene (**2-NCC**).[12−14]



2-NCC

2-NCC has a characteristic electronic spectrum, allowing for UV−vis study,[12,14] and distinct IR bands (due to the substantially different geometry of the singlet and the triplet states),[12] thereby making it amenable to both matrix[12] and time-resolved infrared (TRIR)[13] characterization. These studies show that, in nonpolar solvents and in an argon matrix, **2-NCC** has a triplet ground state and thus can be observed by ESR spectroscopy.[12] However, **2-NCC** has a singlet−triplet energy gap that is close to zero and allows for the experimental observation of both the singlet and the triplet states simultaneously in solution-phase TRIR studies. Indeed, three of us have recently reported that solvent perturbs the singlet−triplet energy gap of **2-NCC**.[15]

There are a number of factors that can affect the energetic ordering of the first singlet and triplet electronic states of a carbene. In the case of an aryl carbene, such as phenylcarbene, ring substituents can have a substantial effect on the singlet−triplet energy gap.[16,17] In this study, we investigate the energetics of the first singlet and triplet electronic states in the analogous phenyl(carbomethoxy)carbene (**PCC**) system using density functional theory methods[18] in order to gauge the effect of phenyl ring substitution on the singlet−triplet energy gap. TRIR methods will be used to provide experimental validation of the computational results.

Computational Methods

All geometries were optimized using the three-parameter hybrid functional B3LYP[19,20] method with the 6-31G* basis set.[21] Analytical second-derivative calculations confirmed each stationary point to be a minimum by yielding zero imaginary vibrational frequencies or a transition state by yielding one imaginary vibrational frequency. These vibrational frequency calculations also provided the zero-point vibrational energy corrections, which were scaled by 0.9806,[22] as well as the thermodynamic corrections necessary to calculate the enthalpies and free energies at 298 K. Furthermore, single-point energy calculations were carried out at the B3LYP level using the 6-311+G** basis set[23] on the B3LYP/6-31G* geometry for all species. All basis sets used six Cartesian d functions. Spin contamination in the triplet states was minimal as $\langle S^2 \rangle$ values were typically between 2.0 and 2.1. In contrast, unrestricted Hartree−Fock based methods suffer from significant spin contamination for similar systems.[15,16] All energies discussed in this paper will be at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory and noted as either an enthalpy or free energy. We should note that we also attempted CBS-QB3[24] calculations on the parent species, and the singlet **PCC** energy calculation could not be completed in 200 CPU hours on an Origin 2000. All calculations were carried out with the Gaussian 98 suite of programs.[25]

Experimental Methods

Unless otherwise noted, materials were obtained from Aldrich Chemical Co. and used without further purification. Acetonitrile and dichloromethane were distilled from CaH_2 before use. Hexane and Freon-113 were dried by passage through a neutral alumina column and stored under argon. All diazo compounds employed in this study were prepared by the diazo-transfer method[26] from their corresponding acetates except 4-(*N*,*N*)-dimethylaminophenyldiazoacetate, which was prepared from its hydrazone as detailed in the Supporting Information. We conducted TRIR experiments following the method of Hamaguchi and co-workers,[27] as described previously.[13]

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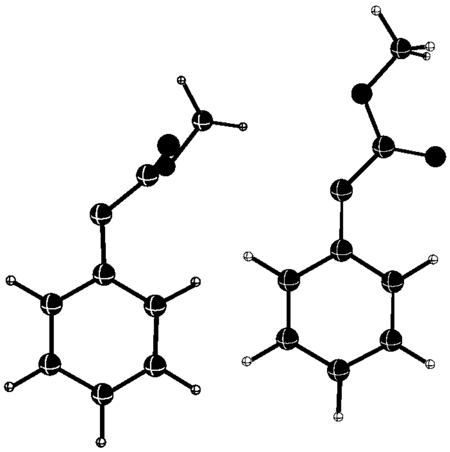


Singlet State Triplet State

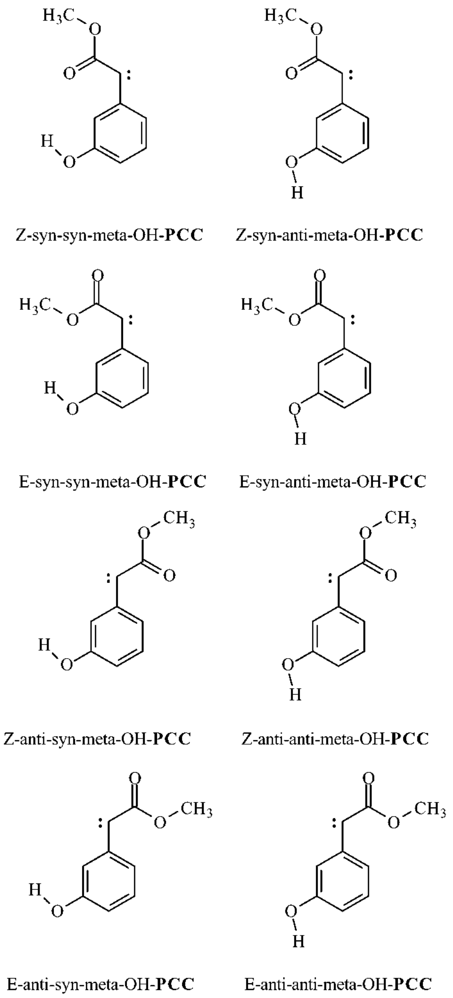
Figure 1. Structure of singlet and triplet **PCC** calculated at the B3LYP/6-31G* level of theory.

Results and Discussion

A. Computational Results. In the analysis of both singlet and triplet substituted phenyl(carbomethoxy)carbenes, one must first resolve the issue of conformational isomerism. The singlet and triplet states of **PCC** have very different molecular geometries.[12,28] The singlet is oriented such that the carbonyl oxygen is perpendicular to the plane defined by the carbene carbon and its adjoining atoms (Figure 1). The triplet carbonyl-carbene is planar with an RCCO dihedral angle of 0.0° (Figure 1). This is common in carbonyl carbene systems.[28] It is well-established that esters (generally) prefer the Z orientation for the CO_2CH_3 moiety,[29] and all conformers examined here have this preferred orientation.

As illustrated in Scheme 1, for triplet *m*-OH-**PCC**, there are three rotational isomerizations that must be taken into account for the planar triplet state. *E* and *Z* isomerism about the C−C single bond between the carbonyl carbon and the carbene carbon must be considered for the planar triplet state species. However, since the C=O bond is perpendicular to the carbene plane in the singlet state, there is no issue of *E* and *Z* isomerism. In both the singlet and the triplet states, one must also consider whether the carbomethoxy group is oriented toward the ring substituent or away from it. When the orientation of the ring substituent is an issue, one must also specify whether the substituent is oriented toward or away from the carbene center for both the singlet and triplet carbenes. In this paper, species will be differentiated by a prefix that will include (where applicable) (1) the isomerism about the carbonyl carbon to carbene carbon single bond (*Z* or *E*), (2) the orientation of the carbene's C=O group (syn or anti), (3) the orientation of the aryl substituent (syn or anti), and (4) the regioisomerism of the substituent (ortho, meta, or para). For many of the substituted phenyl(carbomethoxy)carbenes, these conformers are similar in energy, and each may contribute to the Boltzmann population at a finite temperature.

Scheme 1. Naming Convention for Geometric Isomerism in PCC



We were also concerned about the interconversion of these isomers and, therefore, have calculated the activation barrier for rotation about the ipso-carbon to carbene carbon bond for the parent **PCC**, p-NH_2-**PCC**, and p-NO_2-**PCC**. The rotational barriers (at the B3LYP/6-311+G**//B3LYP/6-31G* level) for the singlet carbenes are 10.3, 11.6, and 12.1 kcal/mol for **PCC** with $X = NH_2$, H, and NO_2, respectively. This is surprising, since it would be expected that the increased resonance interaction of the strong π-donor NH_2 would increase the rotational barrier, but the opposite trend is realized. This is likely due to the ability of the lone pair on the carbonyl oxygen to stabilize the carbene center in the singlet states, as will be discussed later for the para-substituted **PCC** cases. The barrier for rotation in the triplet states is 6.1, 5.3, and 5.0 kcal/mol for p-NH_2-**PCC**, parent **PCC**, and p-NO_2-**PCC**, respectively. These rotational barriers are similar to our recent calculations on substituted phenylcarbenes.[30]

Given the relatively small magnitude of the rotational barriers in these carbenes, we expect that UV photolysis

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Table 1. Calculated Singlet−Triplet Energy Gaps (kcal/mol) for Para-Substituted Phenyl(carbomethoxy)carbene

		B3LYP/6-31G*//B3LYP/6-31G* [a]			B3LYP/6-311+G**//B3LYP/6-31G* [a]		
para substituent	σ_p^+	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)
NH_2	−1.111	−0.1	0.1	0.1	−2.9	−2.7	−2.8
OH	−0.853	2.1[c,d]	2.2[c,d]	2.4[c,d]	−0.5[c,d]	−0.4[c,d]	−0.2[c,d]
OCH_3	−0.648	1.9[c,d]	2.0[c,d]	2.2[c,d]	−1.0[c,e]	−0.9[c,e]	−0.8[c,e]
CH_3	−0.256	4.1	4.2	4.4	1.2	1.4	1.6
F	−0.247	3.9	4.0	4.1	1.4	1.5	1.6
H	0.000	5.0	5.1	5.1	2.4	2.5	2.5
Cl	0.035	5.2	5.3	5.4	2.2	2.4	2.4
NC	*b*	6.3	6.5	6.5	3.9	4.0	4.1
CF_3	0.582	6.7	6.8	6.8	4.4	4.6	4.6
CN	0.674	7.5	7.6	7.8	4.8	4.9	5.2
CHO	*b*	7.5[e,f]	7.7[e,f]	7.8[e,f]	5.4[e,f]	5.5[e,f]	5.6[e,f]
NO_2	0.740	8.0	8.1	8.3	5.8	5.9	6.1
ρ value from LFE analysis		4.0	4.0	4.0	4.2	4.2	4.3

[a] Using the scaled B3LYP/6-31G* zero-point vibrational energy (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] σ_p^+ value is not available. [c] anti-Conformer is the most stable singlet. [d] syn-Conformer is the most stable triplet. [e] anti-Conformer is the most stable triplet. [f] syn-Conformer is the most stable singlet.

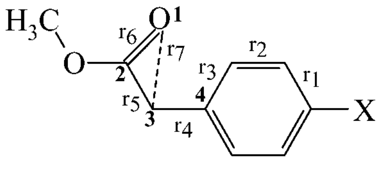
of the carbene precursors will provide sufficient energy to overcome these barriers, thereby sampling all available conformers. Hess et al. have shown that spin and energy relaxation in **2-NCC** occurs in less than 50 ps.[31] Therefore, all relative energies (singlet−triplet energy gaps) will be reported here as the energy difference between the lowest energy triplet and lowest energy singlet conformer for each specific substituent.

1. Para-Substituted PCC. Substitution on the aromatic ring has been shown to have a large effect on the singlet−triplet energy gap for phenylcarbene.[16] It has also been shown[32] that the solvent system used in the ionization of benzoic acids can have a large influence on Hammett ρ values.[33] The commonly accepted explanation for this observation is that if other factors can participate in the stabilization of the benzoate anion (e.g., solvent hydrogen bonding), then the substituent on the benzene ring will be less significant for energetic stabilization. In the case of **PCC** investigated herein, one would expect that, by analogy to the solvent effect example cited above, the participation of the carboxyl group in the stabilization of the carbene center would attenuate the effect of substituents on the singlet−triplet energy gap.

For the triplet states, the planar geometry allows for conjugation with the SOMO, and thus delocalization of the unpaired electron. For the singlet states, the perpendicular orientation of the carbonyl oxygen to the Ph−C−C plane allows for both the donation of the lone pair on oxygen to the empty p-type orbital on the carbene as well as conjugation of the filled sp^2-type orbital to the carbonyl π system. Surprisingly, despite the interaction of the carbomethoxy group with the carbene center, the substituent effect on the singlet−triplet energy gap is quite comparable in **PCC** compared to phenylcarbene. Comparing the two extremes in each system (p-NH_2 and p-NO_2), the $\delta\Delta H_{ST}$ (at 0 K) is 9.6 kcal/mol for phenylcarbene[16] and 8.7 kcal/mol for phenyl(carbomethoxy)carbene. In fact, when ΔH_{ST} is plotted against σ_p^+ for each substituent, the slope (ρ) is 4.2 for **PCC**, as compared to 5.0 for phenylcarbene.[16] This seems to indicate that while the effect of replacing an H in phenylcarbene with a carbomethoxy group may be of some importance, the stabilization imparted by conjugation of the carbene center to the aromatic ring is the dominant factor affecting the relative energy of the singlet and triplet states in the para-substituted species. As can be seen in Table 1, the ρ value for ΔG_{ST} (298 K) for **PCC** is 4.3, quite consistent with the ρ value for ΔH_{ST} (0 K) of 4.2.

Our previous computational study on substituted phenylcarbene[16] indicated that the origin of the substituent effect on the relative energy of the lowest energy singlet and triplet states arose from a preferential interaction with the empty p-type orbital on the carbene carbon in the singlet state as compared to the SOMO aligned with the aromatic π system in the triplet state. This preferential interaction lowers the relative energy of the singlet for strong π-donors (NH_2, OH, OCH_3) and raises it for π-acceptors, such as CN and NO_2. *Thus,* **PCC** *derivatives with the strongest π-donors are calculated to have singlet ground states, with the singlet being 2.8 kcal/mol more stable than the triplet state for the strongest π-donor NH_2.*

Further evidence of this preferential stabilization of the singlet state in **PCC** is provided by an analysis of selected geometric parameters for the para-substituted cases (Supporting Information). Of the parameters selected here, only r_7, the distance between the carbonyl oxygen and the carbene carbon, for the singlet state changes significantly (0.07 Å) as a function of substituent.



para-X-**PCC**

As mentioned earlier, the perpendicular orientation of the carbonyl group to the plane about the carbene carbon allows for donation of the nonbonding electrons on the carbonyl oxygen to the empty p orbital of the singlet state

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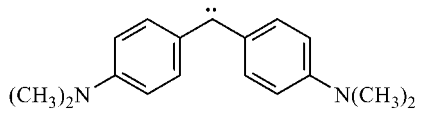
Table 2. Calculated Singlet−Triplet Energy Gaps (kcal/mol) for Meta-Substituted Phenyl(carbomethoxy)carbene

		B3LYP/6-31G*//B3LYP/6-31G* [a]			B3LYP/6-311+G**//B3LYP/6-31G* [a]		
meta substituent	σ_m	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)
NH_2	−0.160	4.9[c,d]	5.1[c,d]	5.2[c,d]	2.6[c,d]	2.8[c,d]	2.9[c,d]
CH_3	−0.069	4.9[d,e]	5.0[c,d]	4.9[d,e]	2.4[d,e]	2.5[c,d]	2.4[d,e]
H	0.000	5.0	5.1	5.1	2.4	2.5	2.5
OCH_3	0.115	5.2[f,g]	5.3[f,g]	5.3[f,g]	2.8[g,h]	2.9[f,g]	2.8[g,h]
OH	0.121	5.5[f,g]	5.6[f,g]	5.8[f,g]	3.1[g,h]	3.3[g,h]	3.3[g,h]
F	0.337	5.8[c,d]	5.9[c,d]	6.0[c,d]	3.6[c,d]	3.7[c,d]	3.8[c,d]
Cl	0.391	5.8[c,i]	5.9[c,i]	6.0[c,i]	3.4[c,i]	3.6[c,i]	3.6[c,i]
CF_3	0.430	6.1[c,i]	6.2[e,i]	6.0[c,i]	3.9[c,i]	4.0[c,i]	3.8[c,i]
CHO	*b*	5.8[j,k]	6.0[j,k]	6.0[j,k]	3.4[j,k]	3.6[j,k]	3.5[j,k]
NC	*b*	6.4[c,i]	6.5[c,i]	6.6[c,i]	4.1[c,i]	4.3[c,i]	4.3[c,i]
CN	0.560	6.6[e,i]	6.7[e,i]	6.8[c,i]	4.3[c,i]	4.4[e,i]	4.5[c,i]
NO_2	0.710	6.7[c,i]	6.9[c,i]	6.9[c,i]	4.4[c,i]	4.6[c,i]	4.6[c,i]
ρ value from LFE analysis		2.3	2.3	2.3	2.5	2.5	2.5

[a] Using the scaled B3LYP/6-31G* zero-point vibrational energy (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] σ_m value is not available. [c] syn-Conformer is the most stable singlet. [d] syn-Conformer is the most stable triplet. [e] anti-Conformer is the most stable singlet. [f] syn,syn-Conformer is the most stable singlet. [g] syn,syn-Conformer is the most stable triplet. [h] anti,syn-Conformer is the most stable singlet. [i] anti-Conformer is the most stable triplet. [j] anti,anti-Conformer is the most stable singlet. [k] syn,anti-Conformer is the most stable triplet.

carbene (as well as delocalization of the carbene sp^2 electrons into the π system of the carbonyl group). This explanation for the geometric preference of the singlet state is further corroborated by the calculated substituent dependence of r_7. When an electron-donating group is in the para position, the electrophilic nature of the carbene center should be mitigated by resonance stabilization. This, in turn, should decrease the demand for electron-donation of the lone pair on the carbonyl oxygen, leading to a longer r_7 contact distance. Electron-withdrawing substituents in the para position should increase the electrophilic nature of the carbene carbon, leading to greater electron donation from the carbonyl oxygen and thus a shorter r_7 contact distance. This is precisely the trend observed.

Previous experimental work has shown 4,4′-bis-(*N*,*N*,*N*′,*N*′)-(dimethylamino)diphenylcarbene to have a triplet ground state.[34] The analogy to the present system, however, is not simple. Steric hindrance in the substituted diphenylcarbene would cause a larger C−C−C bond angle about the carbene center. This would lower the relative energy of the triplet,[35] thus diminishing the effect of resonance stabilization provided by the substituents.



4,4'-bis-(*N*,*N*,*N*′,*N*′)(dimethylamino)diphenylcarbene

On the other hand, electron-withdrawing substituents in **PCC** raise the ΔG_{ST} (298 K). Strong π-acceptors such as NO_2 and CHO raise the ΔG_{ST} (298 K) by ∼3.5 kcal/mol. Inductively electron-withdrawing groups, such as CF_3, raise the singlet−triplet energy splitting, but only by ∼2 kcal/mol. This is in line with the experimental results of Tomioka and co-workers, who predicted that *p*-NO_2-**PCC** has a triplet ground-state by the nonstereospecific trapping of *p*-NO_2-**PCC** with alkenes and by ESR spectroscopy.[36] Additionally, reactivity studies on the parent, **PCC**, indicate that it has a triplet ground state as well.[37]

2. Meta-Substituted PCC. The effect of meta substitution is greatly attenuated compared to para substitution (Table 2). The lack of conjugation to the orbital on the carbene center by the substituents, in fact, results in a higher singlet−triplet energy gap in all cases, except for the *m*-tolylcarbene. Whereas the strong π-donors effected a switch in the ground electronic state for the para-substituted **PCC**, they simply act as inductively electron-withdrawing groups in the meta position and serve to raise the energy of the singlet state, thereby raising the singlet−triplet energy gap. *All of the meta-substituted* **PCC** *carbenes are predicted to have a triplet ground state by >2 kcal/mol.*

A linear free energy analysis has also been performed for the meta-substituted **PCC** (Table 2). The range of values (from 2.4 kcal/mol for *m*-CH_3-**PCC** to 4.6 kcal/mol for *m*-NO_2-**PCC**) is only 2.2 kcal/mol, considerably smaller than in the para-substituted cases. The ρ value in this case is based upon plotting the singlet−triplet energy gaps against σ_m.[38] This leads to a ρ value of 2.5. This value is slightly smaller than the ρ value of 3.3 for a similar analysis applied to substituted phenylcarbene.[16] These results demonstrate that while both inductive and resonance effects are important in these systems, the mesomeric stabilization afforded to the carbene center in the para-substituted **PCC** is the dominant effect. The slightly smaller dependence of the singlet−triplet energy gap in the case of meta-substituted **PCC** compared to phenylcarbene indicates that the carbomethoxy group stabilizes the carbenic center, attenuating the effect of the substituent on the singlet−triplet energy gap.

3. Ortho-Substituted PCC. Ortho substitution provides a complication that has long plagued the physical organic chemist studying aromatic species, as any observed effect is a combination of steric interaction and

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Table 3. Calculated Singlet−Triplet Energy Gaps (kcal/mol) for Ortho-Substituted Phenyl(carbomethoxy)carbene

	B3LYP/6-31G*//B3LYP/6-31G* [a]			B3LYP/6-311+G**//B3LYP/6-31G* [a]		
ortho substituent	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)
NH_2	−1.6[b,c]	−1.4[b,c]	−1.4[b,c]	−4.1[b,c]	−3.9[b,c]	−3.9[b,c]
OH	−1.4[d,e]	−1.2[d,e]	−1.5[d,e]	−3.1[d,e]	−2.9[d,e]	−3.2[d,e]
OCH_3	2.1[d,f]	2.2[d,f]	2.4[d,f]	0.2[d,f]	0.3[d,f]	0.5[d,f]
CH_3	4.2[b,g]	4.3[b,g]	4.5[b,g]	2.1[b,g]	2.2[b,g]	2.5[b,g]
H	5.0	5.1	5.1	2.4	2.5	2.5
F	4.2[g,h]	4.3[g,h]	4.5[g,h]	2.4[g,h]	2.6[g,h]	2.8[g,h]
Cl	6.8[b,g]	6.9[b,g]	7.0[b,g]	4.6[b,g]	4.7[b,g]	4.9[b,g]
NC	7.1[b,g]	7.2[g,h]	7.4[b,g]	5.2[g,h]	5.4[g,h]	5.4[g,h]
CN	7.7[b,g]	7.8[b,g]	8.0[b,g]	5.9[b,g]	6.0[b,g]	6.2[b,g]
CF_3	7.7[b,g]	7.8[b,g]	8.1[b,g]	6.3[b,g]	6.4[b,g]	6.7[b,g]

[a] Using the scaled B3LYP/6-31G* zero-point vibrational energy (and thermal and entropic corrections as appropriate). A positive value of singlet−triplet energy gap indicates that the triplet state is more stable. [b] anti-Conformer is the most stable singlet. [c] syn-Conformer is the most stable triplet. [d] anti,syn-Conformer is the most stable singlet. [e] syn,syn-Conformer is the most stable triplet. [f] anti,anti-Conformer is the most stable triplet. [g] anti-Conformer is the most stable triplet. [h] syn-Conformer is the most stable singlet.

chemical reaction with the proximal substituent as well as resonance and inductive effects.[39] We, therefore, will not offer an LFE analysis of these data, and the singlet−triplet energy gaps are provided in Table 3.

The range spanned by the ΔG_{ST} (298 K) for the ortho species (10.6 kcal/mol) is larger than that observed in the para case. In fact, the strong π-donors NH_2 and OH are predicted to have a singlet ground state with the lowest energy triplet state lying 3−4 kcal/mol higher in energy. The largest ΔG_{ST}, in favor of the triplet state, is calculated for CF_3, which likely arises from a combination of inductive effects destabilizing the singlet state and steric effects limiting conjugation into the aromatic ring.

4. Consideration of Solvation Effects. Polarizable continuum model[40] (PCM) calculations were carried out to assess the effect of solvent on the singlet−triplet energy gap for a few of the para-substituted species. In these calculations, the B3LYP/6-31G* level was used for the complete geometry optimization and vibrational frequency analyses in acetonitrile as a solvent. Single-point energy evaluations were completed at the B3LYP/6-311+G** level, using six Cartesian *d* functions for the basis set. (Once again, multiple conformations were considered for each spin state.) Of the solvents investigated in the TRIR studies (see later), acetonitrile will provide the most profound solvent effect due to its large dielectric constant, and only this solvent was considered for these PCM calculations. The results are presented in Table 4. Inclusion of the acetonitrile solvent model lowers the singlet−triplet energy splitting by ~5 kcal/mol for *p*-NH_2-**PCC** and *p*-OCH_3-**PCC**, making the singlet state even more stable relative to the triplet state. This effect is slightly less (~4 kcal/mol) for *p*-CH_3-**PCC** and parent **PCC**. The implications of these solvent effects will be discussed in more detail below. The calculated stabilization of the singlet state in substituted **PCC** with these PCM calculations is slightly more pronounced than was calculated for unsubstituted **2-NCC**.[15]

Table 4. Calculated Singlet−Triplet Energy Gaps[a] (kcal/mol) for Para-Substituted Phenyl(carbomethoxy)carbene in the Gas Phase and Acetonitrile

	gas phase			acetonitrile[b]		
para substituent	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)	ΔH_{ST} (0 K)	ΔH_{ST} (298 K)	ΔG_{ST} (298 K)
NH_2	−2.9	−2.7	−2.8	−7.9	−7.9	−7.5
OCH_3	−1.0[c,d]	−0.9[c,d]	−0.8[c,d]	−4.3[c,d]	−4.2[c,d]	−3.9[c,d]
CH_3	1.2	1.4	1.6	−1.7	−1.5	−1.3
H	2.4	2.5	2.5	−1.2	−1.0	−1.5

[a] The energy is calculated at the B3LYP/6-311+G** level of theory using the B3LYP/6-31G* geometry and scaled zero-point vibrational energy (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. [c] anti-Conformer is the most stable singlet. [d] anti-Conformer is the most stable triplet.

B. Experimental Results. As has been demonstrated in the case of **2-NCC**,[13,15] experimental insight into carbene singlet−triplet energy gaps may be obtained with TRIR spectroscopy. This analysis relies on comparing the intensities of IR bands due to the singlet carbene relative to those of the triplet carbene. Since the ratio of these signals is directly related to the relative concentrations of singlet to triplet carbene, a corresponding equilibrium constant and, hence, a standard free energy difference (ΔG_{ST}) can be derived. As previously noted,[15] such an analysis requires the following: (1) the two spin states must be equilibrated, (2) IR signals from each spin state must be clearly distinguishable, (3) the ratios of extinction coefficients for these signals must be known, and (4) if solvent effects are to be examined, ΔG_{ST} must be small enough (within ca. ±1 kcal/mol) to allow experimental observation of the solvent perturbation of the equilibrium constant.

Although **2-NCC** fulfilled all of these requirements,[12,13,15] the same is not the case for the **PCC** carbenes of the present study. Most notably, we do not have experimental knowledge of extinction coefficient ratios for the IR bands of **PCC** in the singlet and triplet states or for those of its substituted derivatives. Thus, rather than providing direct measurements of ΔG_{ST} for these carbenes, TRIR experiments are restricted to indicating a very small (within ca. ±1 kcal/mol) or larger (greater than ca. ±2 kcal/mol) ΔG_{ST}, as detailed below.

Tomioka and co-workers have previously studied **PCC** by time-resolved and low-temperature UV−vis absorption spectroscopy, as well as by electron spin resonance (ESR) spectroscopy.[37b] Results were interpreted in terms of the

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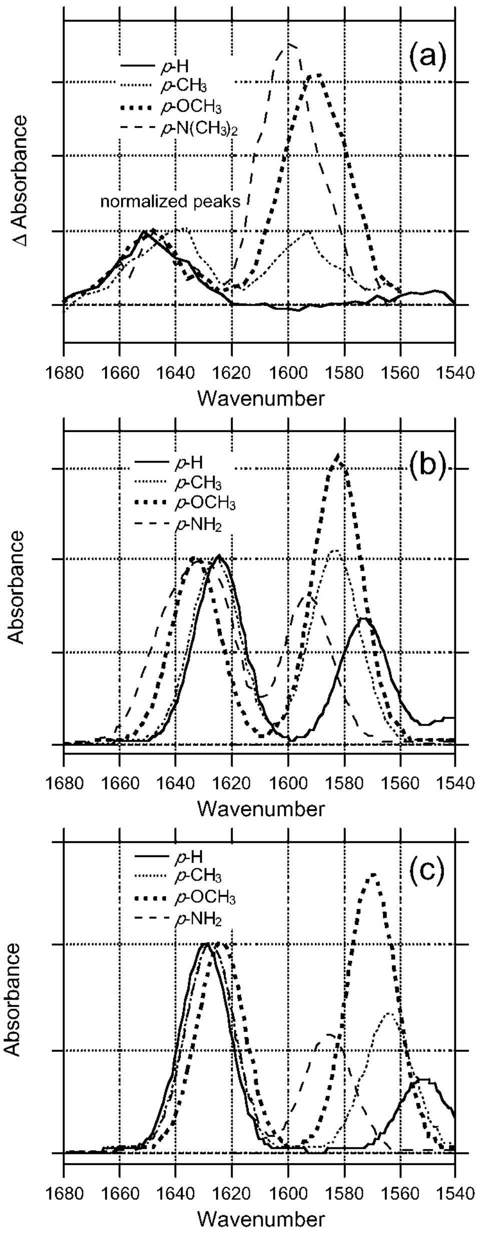

Figure 2. Comparison of experimental TRIR difference spectra observed in Freon-113 (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of the singlet (b) and triplet (c) states of para-substituted **PCC** derivatives in the 1680−1540 cm^{-1} spectral region. TRIR data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96.

carbene having a triplet ground state in rapid equilibrium with the singlet state. In nonaqueous solvents, the lifetime of **PCC** was found to decrease in the presence of oxygen, concurrent with the formation of the corresponding carbonyl oxide. Chiang et al. have also studied **PCC** by transient absorption spectroscopy.[41] They found that in aqueous solutions, the lifetime of **PCC** was unaffected by the presence of oxygen and that a carbonyl oxide was not produced. These results were attributed either to the lower solubility of oxygen in water or to a change in the **PCC** ground state from the triplet state in nonaqueous solutions to the singlet state in water. The latter explanation is consistent with our previous investigations of **2-NCC** that demonstrated that the singlet carbonylcarbene is preferentially stabilized in polar solvents as the result of its increased dipole moment.[15] The magnitude of the observed effect for **PCC** upon changing the dielectric constant from the gas phase to polar acetoni-

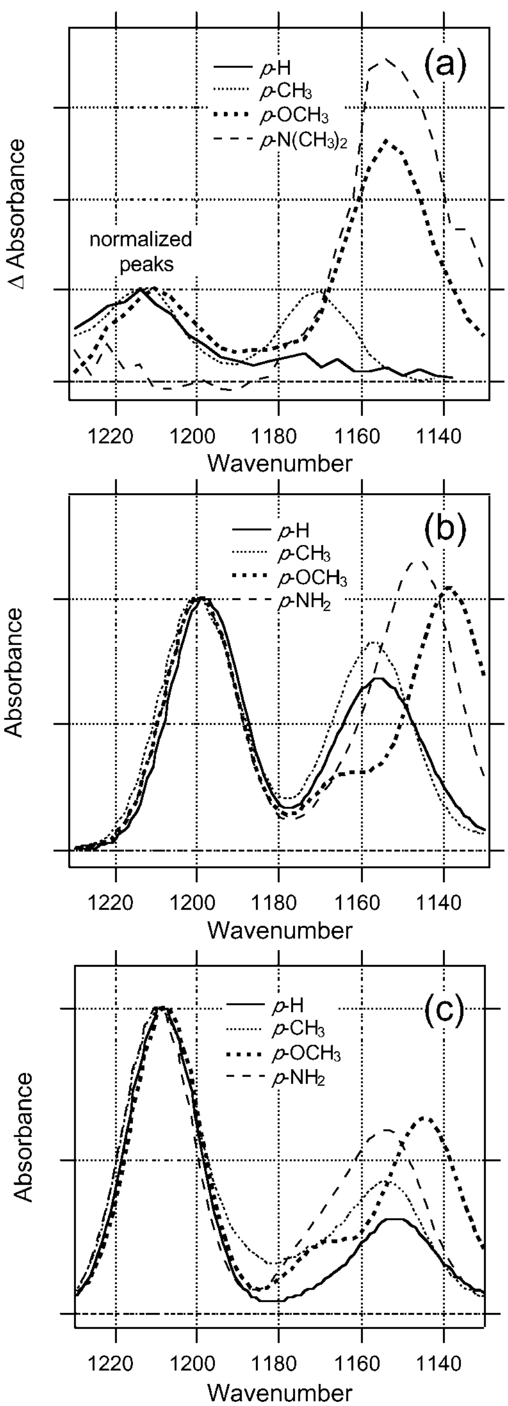

Figure 3. Comparison of experimental TRIR difference spectra observed in acetonitrile (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of the singlet (b) and triplet (c) states of para-substituted **PCC** derivatives in the 1230−1130 cm^{-1} spectral region. TRIR data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96.

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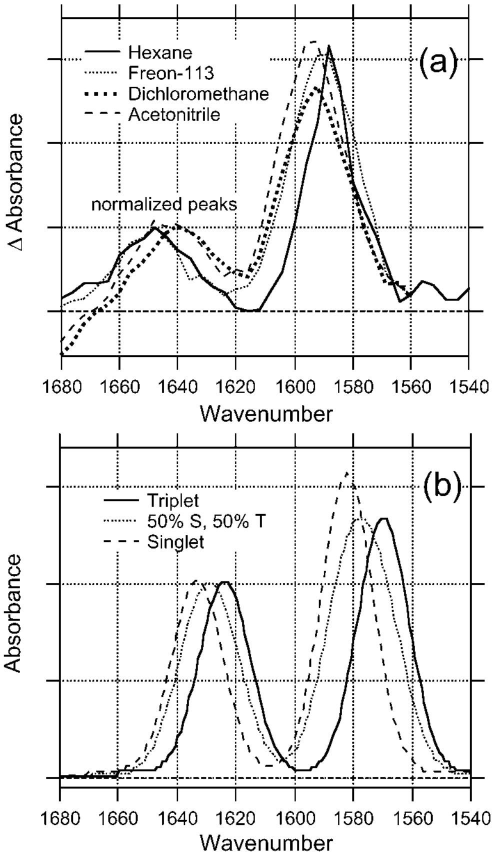

Figure 4. Comparison of the solvent dependence of the experimental TRIR difference spectra (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of varying amounts of singlet and triplet *p*-OCH$_3$-**PCC** (b) in the 1680−1540 cm^{-1} spectral region. TRIR data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96.

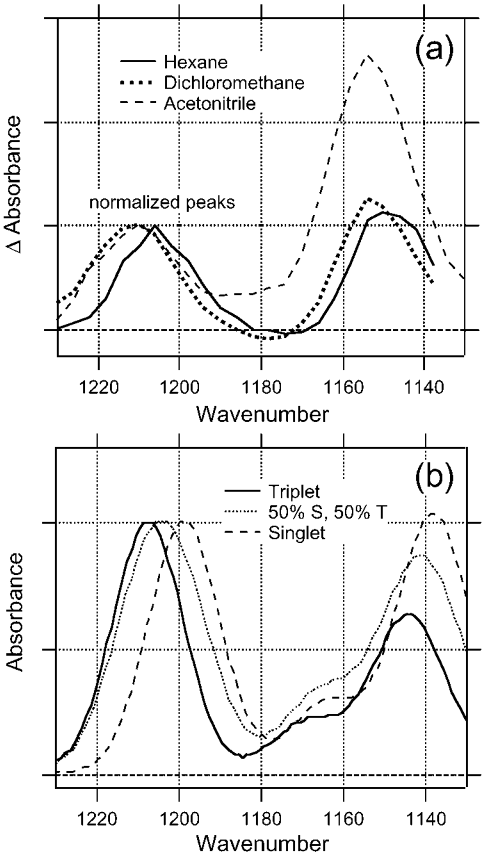

Figure 5. Comparison of the solvent dependence of the experimental TRIR difference spectra (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of varying amounts of singlet and triplet *p*-OCH$_3$-**PCC** (b) in the 1230−1130 cm^{-1} spectral region. TRIR data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96. TRIR data in Freon-113 are not displayed for this spectral region due to interference from strong solvent IR bands.

trile is 3−4 kcal/mol. Bally and Zhu have also studied **PCC** by low-temperature UV−vis and IR spectroscopy.[42] They observe strong IR bands assigned to ^{3}**PCC** at 1660 and 1220 cm^{-1}, in good agreement with our TRIR studies described below.

We have examined a series of para-substituted **PCC** derivatives (H, CH$_3$, OCH$_3$, and N(CH$_3$)$_2$) by TRIR spectroscopy in hexane, Freon-113, dichloromethane, and acetonitrile solutions. Due to complications in the synthesis of 4-aminophenyldiazoacetate, 4-(*N*,*N*)-dimethylaminophenyldiazoacetate was studied experimentally. The electronic properties of *p*-NH$_2$-**PCC** and *p*-N(CH$_3$)$_2$-**PCC** should be very similar, and the calculations for *p*-NH$_2$-**PCC** will be used when discussing the experimental results for *p*-N(CH$_3$)$_2$-**PCC**. Indeed, we have previously shown by calculation that *p*-aminophenylcarbene and *p*-(*N*,*N*)-dimethylaminophenylcarbene have the same singlet−triplet energy gap.[16] As was the case for **2-NCC**,[15] carbene bands are observed in the 1680−1540 cm^{-1} (Figure 2) and the 1230−1130 cm^{-1} (Figure 3) spectral regions following 266 nm laser excitation of the corresponding diazo esters. These experimental data are compared with calculated IR bands of the corresponding singlet and triplet carbenes in Figures 2 and 3. On the basis of the calculations, the experimental bands observed near 1650 and 1590 cm^{-1} are assigned to C=O and aromatic C=C stretching modes, respectively, and those observed near 1210 and 1160 cm^{-1} are assigned as C−O stretching and aromatic C−H bending modes, respectively. All of the observed IR bands for each carbene decay at equal rates within experimental error (±10%), but individual carbene lifetimes vary. For example, in Freon-113 the lifetimes of **PCC**, *p*-CH$_3$-**PCC**, *p*-OCH$_3$-**PCC**, and *p*-N(CH$_3$)$_2$-**PCC** are 1.1, 1.0, 6.7, and 5.0 μs, respectively, at the concentration of diazo precursor present.

The calculations presented above indicate that π-donating para-substituents stabilize the singlet state of **PCC**. Thus, in the *p*-H, -CH$_3$, -OCH$_3$ and -N(CH$_3$)$_2$ series, one would expect to observe more singlet carbene experimentally as one progresses from the H to N(CH$_3$)$_2$ substituents. We do observe changes in relative intensity of the sets of IR signals observed in Figures 2 and 3; however, ratios of extinction coefficients (e.g., C=O modes relative to aromatic C=C modes) are almost certainly changing with substitution. Indeed, the experimental trends in relative intensities observed in Figures 2 and 3 are qualitatively consistent with the trends in calcu-

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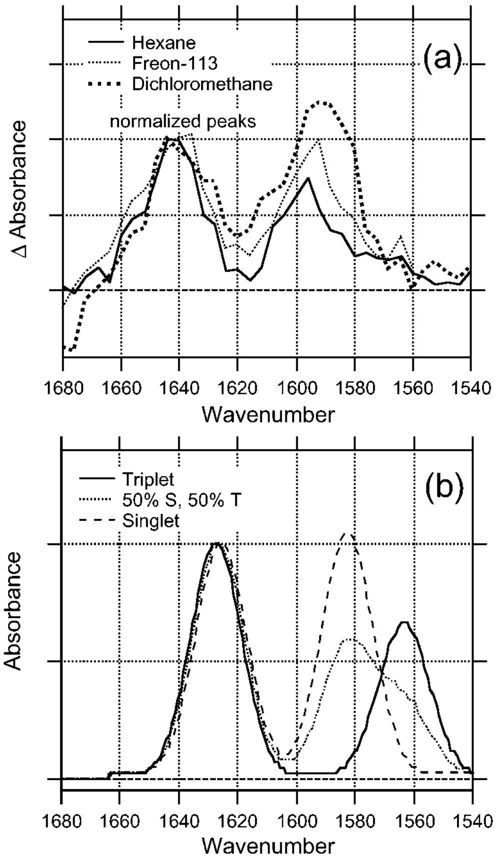

Figure 6. Comparison of the solvent dependence of the experimental TRIR difference spectra (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of varying amounts of singlet and triplet *p*-CH_3-**PCC** (b) in the 1680−1540 cm^{-1} spectral region. TRIR data are averaged over 0−0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96. TRIR data in acetonitrile are not included, because of complications from overlap of bands due to a carbene−acetonitrile ylide. The analogous ylide is not a problem in the case of *p*-OCH_3-**PCC** because the TRIR signals for this system are larger than those of *p*-CH_3-**PCC** by approximately a factor of 3.

lated singlet and triplet carbene IR bands. Note that although the geometries of singlet and triplet para-substituted **PCC** derivatives are calculated to be different, their calculated IR spectra are quite similar, thereby rendering the distinction between a singlet and triplet carbene more difficult in the experimental analysis.

Because of the above complication, we turned to the solvent dependence of the observed IR bands.[43] We cannot detect a solvent dependence on the experimentally observed relative intensities for **PCC** or *p*-$N(CH_3)_2$-**PCC** (Supporting Information) due to insufficient resolution of peaks attributable to the singlet and triplet states, but we do observe a solvent dependence for *p*-OCH_3-**PCC** (Figures 4 and 5) and for *p*-CH_3-**PCC** (Figures 6 and 7).[44] On the basis of these results, we conclude that the singlet−triplet energy gaps in *p*-OCH_3-**PCC** and *p*-CH_3-**PCC** must be small enough to be perturbed to a significant extent by solvent (ΔG_{ST} within ±1 kcal/mol). These results are very consistent with the calculations presented in Table 1.

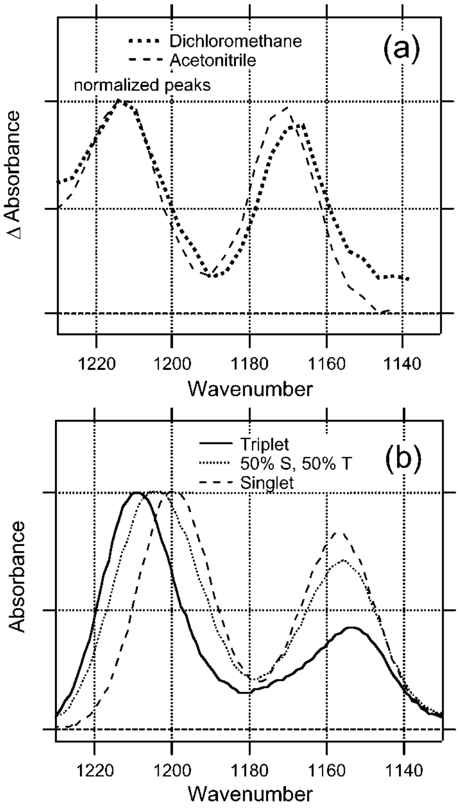

Figure 7. Comparison of the solvent dependence of the experimental TRIR difference spectra (a) and the calculated gas-phase (B3LYP/6-31G*) IR spectra of varying amounts of singlet and triplet *p*-CH_3-**PCC** (b) in the 1230−1130 cm^{-1} spectral region. TRIR data are averaged over 0 to 0.5 μs following 266 nm laser photolysis (5 ns, 1 mJ) of the corresponding diazo ester precursors. For ease of comparison with the solution-phase TRIR data, the calculated signals are treated with a broadening factor of 20 cm^{-1} and scaled by 0.96. TRIR data in Freon-113 are not displayed for this spectral region due to interference from strong solvent IR bands. TRIR data in hexane are not included due to complications from overlap of bands due to an ester produced by carbene C−H insertion. The analogous ester is not a problem in the case of *p*-OCH_3-**PCC**, because the TRIR signals for this system are larger than those of *p*-CH_3-**PCC** by approximately a factor of 3.

In addition, we find no solvent dependence on the observed IR spectra for *m*-CH_3-**PCC** (Supporting Information), again consistent with the computational results (Table 2).

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[43] Solvent effects on carbene singlet−triplet energy gaps have been examined by a combination of kinetics and product analysis for diphenylcarbene and other arylcarbenes: (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (b) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6565. (c) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (d) Langan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1984**, *110*, 521. (e) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543. (f) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966. (g) Adamasu, A. S.; Platz, M. S. *J. Phys. Org. Chem.* **1992**, *5*, 123. (h) Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7011. (i) Garcia-Garibay, M. A. *Tetrahedron Lett.* **1993**, *34*, 8415. (j) Motschiedler, K. R.; Toscano, J. P.; Garcia-Garibay, M. A. *Tetrahedron Lett.* **1997**, *38*, 949. (k) Sung, D. D.; Lim, G. T.; Kim, M. S.; Park, D. K. *Bull. Korean Chem. Soc.* **1995**, *16*, 47.

[44] A caveat here is that solvent may have an effect on IR extinction coefficients for *p*-OCH_3-**PCC** and *p*-CH_3-**PCC**. We addressed this concern in the case of **2-NCC** (ref 15) and concluded that this effect was not substantial.

Conclusions

TRIR methods have been used, in conjunction with DFT calculations, to evaluate the effect of aromatic substitution on the singlet−triplet energy gap for phenyl(carbomethoxy)carbene, **PCC**. Computational results predict that the ground state of **PCC** can be switched from the triplet to the singlet state with substitution on the aromatic ring. Qualitative interpretation of the singlet−triplet energy gap as measured by the effect of solvent in the TRIR experiments agrees with these computational results. When the strongly electron-donating $N(CH_3)_2$ group is in the para position of **PCC**, the calculations demonstrate that the singlet state is strongly favored in the gas phase as well in acetonitrile as a solvent. The observed perturbation of the TRIR spectra of *p*-OCH_3-**PCC** and *p*-CH_3-**PCC** implies a very small ΔG_{ST} for these species. These results agree well with the calculated gas phase ΔG_{ST} of −0.8 and 1.6 kcal/mol for these species, and the calculated solvent perturbation. As well, the lack of solvent effects on the TRIR spectra of *m*-CH_3-**PCC** (implying $\Delta G_{ST} > 2$ kcal/mol) is in agreement with our calculations, which predict that the singlet−triplet energy separation is 2.4 kcal/mol in the gas phase.

LFE analyses are also presented for the para- and meta-substituted species. There is a slight decrease in the ρ value for the relationship of ΔH_{ST} (0 K) in **PCC** compared to that of phenylcarbene.[16] There is, though, a good linear correlation between ΔG_{ST} and σ_p^+, implying that, as in the case of phenylcarbene, interaction of the aromatic system with the empty p orbital on the carbene center in the singlet state is the most influential factor determining the observed substituent effect. Ortho-substitution is predicted to have a larger effect on the singlet−triplet energy gap than para-substitution. This is due to a combination of steric and mesomeric interactions with the carbene center. Perhaps the most dramatic example of this is in *o*-CF_3-**PCC**. Here, the predicted ΔG_{ST} is larger than in the para-substituted species. The steric interaction of the carbene center with CF_3 in this species hinders conjugation of the carbene to the aromatic ring. Since the singlet has been shown to benefit more from this stabilizing conjugation, the relative energy of this species is increased with respect to the triplet, leading to the large ΔG_{ST}.

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Supporting Information Available: IR, NMR, UV−vis, and MS spectra of the diazo compounds, along with the calculated energies, enthalpies, free energies, Cartesian coordinates, and harmonic frequencies for all species as well as TRIR spectra for *p*-$N(CH_3)_2$-**PCC** and *m*-CH_3-**PCC**. Selected geometric parameters for singlet and triplet **PCC** derivatives are provided. LFE plots are also included. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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