Heterogeneous Substitution Effects in Chlorocyanomethyl Radical and Chlorocyanocarbene

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ABSTRACT: We report a photoelectron-imaging investigation of the chlorocyanomethyl radical (CHClCN) and the corresponding carbene (CClCN). The results are discussed in comparison with the corresponding dichloro- and dicyano-substituted species, focusing on the divergent effects of the halogen and pseudohalogen (CN) substitutions. A cooperative (captodative) interaction of the π -donor Cl and π -acceptor cyano groups favors the increased stability of the CHClCN radical, but a competition of the two substituents is observed in the singlet-triplet splitting of the carbene. The vertical detachment energy (VDE) of CHClCN⁻ is determined to be 2.39 \pm 0.04 eV, with the broad photoelectron band consistent with the significant geometry change predicted by theory for the detachment transition. The adiabatic electron affinity of CHClCN, EA = 1.86 \pm 0.08 eV, is estimated on the basis of the experimental VDE and the computed difference between the VDE and EA values. This result allows the calculation of the bond dissociation energy of chloroacetonitrile, DH₂₉₈(H-CHClCN) = 87.0 \pm 2.7 kcal/mol. Photoelectron imaging of CClCN⁻ reveals two main transitions,



assigned to the singlet $({}^{1}A')$ and triplet $({}^{3}A'')$ states of the CCICN carbene. The respective VDEs are 2.76 ± 0.05 and 3.25 ± 0.05 eV. The experimental results are in good agreement with the theoretically predicted singlet-triplet vertical energy gap at the anion geometry, but inconclusive with regard to the adiabatic singlet-triplet splitting in CCICN. Consistent with the experimental findings, ab initio calculations using the spin-flip approach in combination with the coupled-cluster theory, indicate that the ${}^{1}A'$ and ${}^{3}A''$ states are nearly degenerate, with the singlet state lying adiabatically only ~0.01 eV below the triplet.

1. INTRODUCTION

Methyl radicals (\cdot CR₁R₂R₃) and carbenes (:CR₁R₂) are fundamentally interesting species that play important roles as intermediates in chemical reactions. Their structures and stabilities vary depending on the properties of the substituents (R). The radical stability, related to the bond dissociation energy (BDE) of the corresponding closed-shell molecule, ΔH_{298} (H–CR₁R₂R₃), is affected by resonance and inductive effects of the substituents.^{1,2} The canonical picture of a carbene is even more intricate, due to the existence of two nearly degenerate nonbonding σ and π orbitals on the central carbon atom occupied by two electrons.^{3,4} The neighboring atoms affect the energy difference between these orbitals, determining the electron configuration (... $\sigma^2 \pi^0$ or ... $\sigma^1 \pi^1$) and the multiplicity of the ground state of the carbene, as well as the magnitude of the singlet-triplet splitting.

Radicals and carbenes are well suited for studies using anion photoelectron spectroscopy.⁵ The precursor anions can be formed in the gas phase using the well-documented H⁺ or H₂⁺ abstraction reactions of O⁻ with the corresponding closed-shell molecules.^{6,7} With regard to carbenes, photoelectron spectroscopy affords an additional key advantage of accessing both the singlet and triplet states of the neutral species. For a canonical carbene, the anion lowest-energy electron configuration is ... $\sigma^2 \pi^1$ and the lowest singlet and triplet states of the neutral are accessed by detachment from the respective π and σ orbitals.³ (Photodetachment from the σ orbital also accesses the openshell ... $\sigma^1 \pi^1$ singlet state, which will be explicitly referred to as "the open-shell singlet". The short-hand designation "the singlet" is reserved for the closed-shell $...\sigma^2 \pi^0$ singlet state.) With this in mind, photoelectron imaging proves to be especially advantageous, because the π and σ orbitals are generally expected to yield distinct photoelectron angular distributions (PAD) reflecting the symmetry properties of the nonbonding orbitals.^{8,9} Thus, the multiplicity and energy ordering of the electronic states of carbenes can be assigned (in some cases) on the basis of a simple examination of the PADs.

In this work, we focus on the effects of Cl and CN substituents on the properties of doubly substituted methyl radicals and carbenes. The inductive effects attributed to both substituents increase the electron affinity (EA). In addition, π -electron donation by halogens increases the energy splitting between the nonbonding σ and π orbitals in chlorocarbenes, favoring a singlet ground state.^{10,11} The cyano group is often referred to as a pseudohalogen, due to its high electronegativity and monovalent reactivity. However, although true halogens act as π electron donors, the cyano group does not. Instead, conjugation of its π system with the nonbonding 2p (π) orbital on the central carbon stabilizes the triplet state of the carbene.^{3,4,12,13} For this reason, in contrast to HCCl and

Received:May 29, 2013Revised:September 18, 2013Published:September 19, 2013

The Journal of Physical Chemistry A

 $\rm CCl_2$, the corresponding cyano-substituted carbenes, HCCN and $\rm C(CN)_2$, have triplet ground states. 3,14,15

We report a study of the heterogeneously substituted methyl radical, CHCICN, and the corresponding carbene, CCICN. We show that the π -donor halogen and π -acceptor cyano groups have a cooperative (captodative) effect on the mixed radical stability and, to the contrary, competing effects on the singlet—triplet splitting in the mixed carbene. We use negative-ion photoelectron imaging to examine the properties of CHCICN and CCICN and compare the findings to the corresponding dichloro and dicyano radicals and carbenes, focusing on the divergent effects of the halogen and pseudohalogen (CN) substitutions.

2. EXPERIMENTAL AND THEORETICAL METHODS

The experiments were performed using the negative-ion photoelectron imaging spectrometer described in detail elsewhere.¹⁶ In brief, a precursor gas mixture at a backing pressure of 20–30 psi is expanded into a vacuum through a pulsed supersonic nozzle (General Valve, Series 99) operated at a 50 Hz repetition rate. The expansion is crossed with a collimated 1 keV electron beam. The resulting anions are pulse-extracted into a linear Willey–McLaren¹⁷ time-of-flight mass spectrometer and accelerated to 2.5 keV. The mass-selected anions are photodetached within a velocity-map¹⁸ imaging¹⁹ assembly using linearly polarized laser pulses timed to coincide only with the ions of interest. The second or third harmonics of a Spectra Physics, Inc. Lab-130 Nd:YAG (yttrium aluminum garnet) laser (10 ns pulse duration, 20 mJ/pulse at 532 nm, 5 mJ/pulse at 355 nm) were used to detach electrons.

The photodetached electrons are accelerated by a series of velocity-mapping electrodes onto a 40 mm position sensitive microchannel plate detector coupled to a P43 phosphor screen (Burle, Inc.). The resulting images are recorded by a charge-coupled device camera. Typically, $\sim 10^6$ experimental cycles are accumulated for each reported image. The images are analyzed using the inverse Abel transform implemented in the BASEX program²⁰ to yield the complete three-dimensional photo-electron distributions.²¹ The energy scale in the resulting spectra is calibrated using the well-known photodetachment transition of O⁻.^{22,23}

To generate the CClCN⁻ and CHClCN⁻ ions studied in this work, the precursor chloroacetonitrile, CH₂ClCN, vapor was seeded in an N_2O or O_2 carrier gas. Dissociative electron attachment to N₂O produced O⁻ radical anions, which in turn reacted with chloroacetonitrile to form chlorocyanomethylide (CHClCN⁻) and chlorocyanocarbene (CClCN⁻) anions via the respective H^+ and H_2^+ abstraction reactions. A representative mass-spectrum of the anions generated with CH₂ClCN seeded in N₂O is shown in Figure 1a. All chlorinecontaining anions yield two dominant mass-spectral peaks each, with approximate 3:1 intensity ratios reflecting the natural abundances of the main chlorine isotopes, ³⁵Cl and ³⁷Cl. The CClCN⁻ anion is expected at 73 and 75 amu. The corresponding peaks in Figure 1a clearly violate the expected intensity ratio and most of the 75 amu intensity is attributed to a different species, possibly $HNO^- N_2O$. The 73 amu peak was used for the experiments on CClCN⁻. The mass spectra in Figure 1 are plotted on arbitrary intensity scales. Although the 73 amu peak appears small in Figure 1a, sufficiently strong photodetachment signal was observed, as evidenced by the results in section 4.



Figure 1. Representative time-of-flight mass spectra for (a) CH_2ClCN/N_2O and (b) CH_2ClCN/O_2 reaction gas mixtures. All chlorine-containing anions yield two dominant mass-spectral peaks each, due to two naturally abundant chlorine isotopes, ³⁵Cl and ³⁷Cl. The m/z = 74 and 76 amu peaks correspond to CHClCN⁻, whereas m/z = 73 and 75 amu correspond to CClCN⁻. Most of the 75 amu intensity, however, is attributed to a different species, possibly HNO⁻. N₂O.

Similarly, CHClCN⁻ is expected at m = 74 amu, with a lessintense satellite peak at 76 amu. When a CH₂ClCN/N₂O reaction mixture is used (Figure 1a), the primary CHClCN⁻ peak (74 amu) overlaps with the NO⁻·N₂O or N₃O₂⁻ ions.^{24,25} Therefore, an O⁻ reagent source other than N₂O was necessary for experiments on CHClCN⁻. The mass-spectrum displayed in Figure 1b was obtained using O₂ instead of N₂O. The 74 amu ions observed under these conditions were the target of CHClCN⁻ experiments.

Electronic-structure calculations involving geometry optimizations at the coupled-cluster level of theory with single, double (and triple) excitations, CCSD and CCSD(T), were performed using the Gaussian 09 suites of programs.²⁶ The geometries for the anion and neutral ground and excited states were optimized, with the normal-mode analysis used to confirm that the structures corresponded to true potential minima.

The low-lying electronic states were explored using the equation-of-motion (EOM) spin-flip (SF) methodology^{27–30} combined with the coupled-cluster theory, including diagonal triples corrections (dT).³¹ All EOM-XX-CCSD(dT) calculations (XX = SF or IP) were carried out using the Q-Chem 4.0 software package.³²

3. CHLOROCYANOMETHYL RADICAL

The 355 and 532 nm photoelectron images of CHClCN⁻ are shown in Figure 2 alongside the corresponding spectra. All spectra in this work are plotted with respect to electron binding energy eBE = $h\nu$ – eKE, where $h\nu$ is the photon energy and eKE is electron kinetic energy.

3.1. Vertical Detachment Energy of Chlorocyanome-thylide. The 355 nm photodetachment band is fitted with a Gaussian, shown in Figure 2a as a gray curve. The fit used the part of the experimental spectrum falling within the full-width-

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Figure 2. Photoelectron images and spectra of $CHClCN^-$ obtained at (a) 355 nm and (b) 532 nm. The gray curves are fits to the experimental data. The red curve in (b) is the "clean" spectrum obtained using the low-pass filter Fourier analysis, as described in the text.

at-half-maximum interval. The maximum position of the fitted Gaussian is assigned as the vertical detachment energy of CHClCN⁻, VDE = 2.39 ± 0.04 eV. The origin of the band, corresponding to the adiabatic EA of the neutral radical, is not immediately apparent.

The 532 nm photodetachment band (Figure 2b) corresponds to the same transition. To account for the low-eKE effects expected near the energetic cutoff at eBE = $h\nu$ = 2.33 eV, the 532 nm spectrum was fitted with the modified Gaussian function (shown in gray):

$$P(eBE) = C(h\nu - eBE)^{1/2} \exp[-(eBE - VDE)^2/w^2]$$
(1)

where *w* is a width parameter and *C* is a normalization coefficient. Equation 1 assumes a Gaussian Franck–Condon profile and approximates the electronic cross-section scaling using a Wigner-like³³ prefactor $(h\nu - eBE)^{1/2} = eKE^{1/2}$, where the 1/2-power dependence reflects the assumed contribution of s partial waves. This assumption is strictly justified only for low-eKE electrons,³⁴ but previous modeling with similar approaches was successful in describing broad photoelectron bands.^{35,36}

Due to the low-eKE intensity scaling, the maximum position of the 532 nm spectrum is shifted with respect to the VDE determined from the 355 nm spectrum. It is for this reason that the 355 nm spectrum provides for a more reliable determination of the VDE. Hence, the 532 nm spectrum in Figure 2b was fitted using eq 1 by adjusting w for best fit, whereas the VDE value was fixed at that determined from the 355 nm spectrum. The resulting fit curve is overlaid with the experimental spectrum in Figure 2b.

Calculations for the ground states of CHClCN⁻ and CHClCN yielded the equilibrium geometries shown in Figure 3, with the bond lengths and angles given in the caption. The structures were optimized²⁶ at the CCSD level of theory using Dunning's augmented correlation-consistent polarized valence triple- ζ basis set (aug-cc-pVTZ). The significant geometry change expected upon electron detachment from CHClCN⁻ (nonplanar pyramidal to trigonal planar) is consistent with the broad and congested photoelectron bands in Figure 2.



Figure 3. CCSD/aug-cc-pVTZ optimized geometries of CHClCN⁻ and CHClCN. Anion structural parameters: $R_{C-C} = 1.415$ Å, $R_{C=N} = 1.165$ Å, $R_{C-CI} = 1.840$ Å, $R_{C-H} = 1.086$ Å, $\angle CI-C-C = 110.1^{\circ}$, $\angle CI-C-H = 105.8^{\circ}$, $\angle C-C-N = 174.5^{\circ}$, dihedral(CI-C-C-N) = 125.9^{\circ}, dihedral(H-C-C-N) = -116.8°. Neutral (planar): $R_{C-C} = 1.396$ Å, $R_{C=N} = 1.172$ Å, $R_{C-CI} = 1.699$ Å, $R_{C-H} = 1.076$ Å, $\angle CI-C-C = 120.4^{\circ}$, $\angle CI-C-H = 117.7^{\circ}$, $\angle C-C-N = 179.1^{\circ}$, dihedral(CI-C-C-N) = 180°.

The VDE of CHClCN⁻ and the EA of CHClCN were obtained from single-point calculations with a variety of methods and basis sets, using the optimized anion and neutral geometries shown in Figure 3. In all calculations, the VDE is defined as the energy difference between the neutral and anion states at the anion equilibrium geometry, whereas the EA is the energy difference between the respective neutral and anion equilibrium structures. The results are summarized in Table 1. For the couple-cluster calculations, the Hartree–Fock (HF) orbital bases were used by default. However, some of the CCSD values in Table 1 were calculated³² using unrestricted B3LYP orbitals, to minimize the effect of spin-contamination. In addition, single-point EOM-IP-CCSD calculations³⁰ were carried out³² for the optimized structure of the anion; the resulting VDE values are also included in Table 1.

The best (highest-level/largest basis) estimates of both the VDE and the EA were obtained from the CCSD(T)/aug-cc-pVTZ calculations. The corresponding VDE = 2.40 eV agrees perfectly with the experimental result, VDE = 2.39 ± 0.04 eV.

3.2. Electron Affinity of the Chlorocyanomethyl Radical. The adiabatic EA of CHClCN cannot be determined directly from the data in Figure 2, because the band origin is not obvious in the spectra. An estimate using the following approximation can be obtained on the basis of the experimentally determined anion VDE = $2.39 \pm 0.04 \text{ eV}$:¹⁰

$$EA \approx VDE + (EA_{calc} - VDE_{calc})$$
(2)

where EA_{calc} and VDE_{calc} are the adiabatic EA of CHClCN and the VDE of CHClCN⁻, respectively, derived from theory calculations. Equation 2 assumes that the errors in the calculated EA and VDE values are similar; i.e., the shift between the VDE and adiabatic EA (attributed to the anionneutral geometry difference) can be reliably evaluated by theory.

As seen in Table 1, both EA_{calc} and VDE_{calc} vary substantially depending on the theory level and the basis set used. However, per eq 2, the EA estimate is dependent on the difference between the two computed properties, rather than their individual values, and the variation of the difference is less significant. In the following analysis, we will use the best theory result, CCSD(T)/aug-cc-pVTZ, which is also in agreement with the experimentally determined VDE. Substituting the corresponding value of $\text{EA}_{\text{calc}} - \text{VDE}_{\text{calc}} = -0.53 \text{ eV}$ into eq 2, the electron affinity of chlorocyanomethyl radical is determined as EA = $1.86 \pm 0.08 \text{ eV}$. The error bars are a combination of the experimental uncertainty in the VDE and the deemed to be

Table 1. Adiabatic Electron Affinity (EA) of CHClCN and Vertical Detachment Energy (VDE) of CHClCN⁻ Determined Using Different Methods and Basis Sets (All Values in Electronvolts)

method	basis set	EA	VDE	$EA_{calc} - VDE_{calc}$
B3LYP ^a	aug-cc-pVDZ	1.93	2.44	-0.51
	aug-cc-pVTZ	1.89	2.46	-0.57
	6-311++G**	1.91	2.46	-0.57
	6-311++G(3df,3pd)	1.87	2.46	-0.59
CCSD^a	aug-cc-pVDZ ^b	1.70	2.19	-0.49
	aug-cc-pVTZ	1.75	2.32	-0.57
	6-311++G** ^b	1.47	2.05	-0.58
	6-311++G(3df,3pd) ^b	2.30		
$CCSD(T)^{a}$	aug-cc-pVDZ ^b	1.78	2.22	-0.44
	aug-cc-pVTZ	1.87	2.40	-0.53
	6-311++G** ^b	1.53	2.06	-0.53
EOM-IP-CCSD ^b	aug-cc-pVDZ		2.29	
	6-311++G**		2.20	
	6-311++G(3df,3pd)		2.46	
experiment		1.86 ± 0.08^{c}	2.39 ± 0.04	

^{*a*}The B3LYP, CCSD, and CCSD(T) values are calculated as the difference between the energies of the neutral and the anion (zero-point vibrational energy corrections are not included). For VDE calculations, both the neutral and the anion energies were computed for the anion equilibrium geometry. For adiabatic EA calculations, the respective neutral and anion equilibrium geometries were used. The geometries were optimized at the CCSD/aug-cc-pVTZ level (Figure 3). Theory values in bold correspond to the highest theory level and basis set. ^{*b*}When indicated, B3LYP orbitals were used as the basis for single-point coupled-cluster calculations to reduce the effect of spin contamination. In all other cases, the canonical HF orbitals were used. The absolute energy difference between the two approaches is ≤ 0.02 eV for the computed EA and VDE values and ≤ 0.01 eV for EA_{calc} – VDE_{calc}. ^{*c*}Estimated value determined using eq 2 and the CCSD(T)/aug-cc-pVTZ result for EA_{calc} – VDE_{calc}.

on the order of chemical accuracy $(\sim 1 \text{ kcal/mol})^{37}$ uncertainty of the theory result. Thus determined EA value and the corresponding confidence interval are indicated in Figure 2. This result constitutes the first determination of the CHClCN radical EA using spectroscopic data.

To further support the above EA determination, the low-pass filter Fourier analysis, described previously,³⁸ was performed on both spectra shown in Figure 2. The "clean" spectra (shown only for 532 nm spectrum in red) revealed the onset of the transition at approximately 1.8 eV, as determined by the signal rising above the noise level, in agreement with the above EA estimate. The same analysis yielded a vibrational period of 450 \pm 50 cm⁻¹, which we attribute to the umbrella mode excited upon photodetachment due to the anion-neutral geometry difference.

3.3. C–H Bond Dissociation Energy of Chloroacetonitrile. The above determination of EA(CHClCN) makes it possible to evaluate the C–H bond enthalpy of chloroacetonitrile using the general acidity/electron affinity cycle:¹

$$DH_{298}(R-H) = \Delta_{acid}H_{298}(RH) + EA(R) - IE(H)$$

+ [thermal corrections] (3)

In this equation, $\Delta_{acid}H_{298}(RH)$ is the gas-phase acidity of the closed-shell molecule, EA(R) is the electron affinity of its radical, and IE(H) = 313.6 kcal/mol (13.60 eV) is the ionization energy of atomic hydrogen.³⁹ Using the published acidity of chloroacetonitrile, $\Delta_{acid}H_{298}(CH_2CICN) = 357.7 \pm 2.0 \text{ kcal/mol},^{40}$ and the EA of the corresponding radical, EA(CHCICN) = 1.86 \pm 0.08 eV = 42.9 \pm 1.8 kcal/mol, as determined above, while neglecting the small (usually ~0.3 kcal/mol) thermal corrections term, we find the C–H BDE of chloroacetonitrile to be DH₂₉₈(H–CHCICN) = 87.0 \pm 2.7 kcal/mol.

The BDE is related to the stability of the resulting radical, with smaller DH_{298} values corresponding to greater radical stability. The above BDE for chloroacetonitrile is smaller than

the C–H bond energies of many closed-shell molecules. For comparison, the BDEs of several halogen and cyano-substituted methanes are summarized in Table 2. $^{1,41-43}$ The corresponding

Table 2. C–H Bond Dissociation Energies, DH ₂₉₈ (R–H	H),
and the Corresponding Radical Stabilization Energies, 1	RSE,
of Substituted Methanes (All Values in kcal/mol)	

compound	DH ₂₉₈	ref	RSE ^a	
CH_4	104.9 ± 0.4	1	0	
	Fluorome	ethanes		
CH ₃ F	103.2 ± 1.0	41	1.7 ± 1.1	
CH_2F_2	106.4 ± 0.7	41	-1.5 ± 0.8	
CHF ₃	106.7 ± 1.0	41	-1.8 ± 1.1	
	Chlorome	ethanes		
CH ₃ Cl	100.1 ± 0.6	41	4.8 ± 0.7	
CH_2Cl_2	95.7 ± 0.5	41	9.2 ± 0.6	
CHCl ₃	93.8 ± 0.6	41	11.1 ± 0.7	
Cyanomethanes				
CH ₃ CN	94.2 ± 2.0	42, 43	10.7 ± 2.0	
$CH_2(CN)_2$	88.7 ± 2.1	43 ^b	16.2 ± 2.1	
$CH(CN)_3$	unknown			
Chlorocyanomethane				
CH ₂ ClCN	87.0 ± 2.7	this work	17.9 ± 2.7	

"The radical stabilization energies are calculated as RSE(R–H) = $DH_{298}(CH_3-H) - DH_{298}(R-H)$." The C–H BDE of $CH_2(CN)_2$ was determined in ref 43 assuming IE(H) = 315.1 kcal/mol.⁵⁰ The BDE given here reflects the corrected value of 313.6 kcal/mol.³⁹ The revised $DH_{298}[H-CH(CN)_2]$ value is within the uncertainty range of the original determination.

radical stabilization energies (RSE), calculated as the difference between the BDE of methane and that of the corresponding substituted molecule, are also included in the table.

The relative stabilities of the substituted radicals are determined by a combination of inductive and resonance effects. Both halogens and CN are strong electron-withdrawing



Figure 4. Photoelectron images and spectra of (a) CCl_2^- at 355 nm, (b) $CClCN^-$ at 355 nm, and (c) $C(CN)_2^-$ at 266 nm (data from earlier work).¹⁵ Bands are fit with Gaussian or modified Gaussian functions (see the text for details). The singlet bands (S) are fit with green curves and correspond to the respective ¹A₁ states of CCl_2 and $C(CN)_2$ and the ¹A' state of CClCN. The triplet bands are fit with blue curves and correspond to the ³B₁ states of CCl_2 and $C(CN)_2$ and the ³A'' state of CClCN.

groups with respect to the molecular σ system, destabilizing the electron-deficient radical center. However, with respect to the π system, halogens act as electron donors, and the CN group stabilizes the radical via resonance interaction, by donating its π system to the extended molecular framework.^{1,2} It is for this last reason that the BDEs of CH₃CN and CH₂(CN)₂ are both progressively smaller, in comparison to the value for methane.^{42,43}

Although the extent of the π donation or resonance stabilization depends on the overlap between the orbitals on the substituent and the radical center,² the magnitude of the inductive effect depends on the substituent's electronegativity. In fluoro-substituted methanes, the σ withdrawing and π donation effects are nearly balanced out, as all four CH_{4-n}F_n species (n = 0-3) have similar C–H BDEs (Table 2). However, replacing F with less electronegative Cl results in an increased stability of the chloromethyl radicals, as reflected in the RSE(CH_{4-n}Cl_n) values.

The C–H BDE of CH₂ClCN, determined in this work, corresponds to an RSE of 17.9 ± 2.7 kcal/mol. This is almost twice as large as the corresponding CH₂Cl₂ value (9.2 ± 0.6 kcal/mol),⁴¹ but similar to that for CH₂(CN)₂ (16.2 ± 2.1 kcal/mol).⁴³ Moreover, the effect of the mixed CN and Cl substitution on the radical stability is comparable to (if not greater than) the sum of the separate single substitutions, RSE(CH₃CN) + RSE(CH₃Cl) = 15.5 ± 2.1 kcal/mol. These findings suggest that the mixed CHClCN radical benefits from a cooperative interaction of the unsaturated π resonance attributed to CN, and the π donation due to Cl. A captodative combination of these effects yields a radical of increased stability.⁴⁴

4. CHLOROCYANOCARBENE

The results for CClCN⁻ (355 nm) are shown in Figure 4b, where they are presented in comparison with the corresponding data for (a) CCl_2^{-} (355 nm)⁴⁵ and (c) $C(CN)_2^{-}$ (266 nm).¹⁵ The results in (b) are new, but the "reference" data in (a) and (c) are not. The CCl_2^{-} data set (a) is similar to the one reported by us recently, albeit in a different context.⁴⁵ These imaging results are fully consistent with the higher-resolution photoelectron spectrum reported by Lineberger and coworkers.¹¹ The $C(CN)_2^{-}$ data in (c) are adopted from our earlier work.¹⁵

The bulk of the following discussion (sections 4.2–4.6) is concerned only with the new CClCN⁻ results, and the comparison to CCl_2^- and $C(CN)_2^-$ is found in section 5.2. However, first (in section 4.1) we present a brief discussion of the qualitative insight gained from the CCl_2^- data, which helps set the stage for the assignment of the $CClCN^-$ bands.

4.1. Carbene Anion Imaging on the Example of Dichlorocarbene. The CCl_2^- data in Figure 4a is a particularly instructive case of carbene spectroscopy, because the characters of the σ and π carbene orbitals are immediately apparent in the PADs of the two clearly separated $CCl_2^$ photodetachment bands. Because the σ orbital (nominally an in-plane sp² hybrid) is totally symmetric with respect to the symmetry operations of the molecular point group,⁸ and because of its significant s character,⁴⁵ the σ^{-1} PAD (triplet carbene) is notably parallel with respect to the laser polarization axis (vertical in Figure 4). On the other hand, the PAD of the π^{-1} channel, (singlet carbene) is perpendicular, characteristic of a p-like initial state.

The above qualitative analysis is not unique to dichlorocarbene. In general (and with due caution), in the moderateeKE regime, we expect photodetachment from the σ nonTable 3. Calculated VDEs of CClCN⁻ Corresponding to Detachment to the ¹A', ³A", and ¹A" States of the Neutral, the Adiabatic EAs of the Singlet and Triplet Carbene, and the Corresponding Values of Adiabatic Singlet–Triplet Splitting $(\Delta E_{S-T})^a$

		VDE		adiabat	ic EA	adiabatic
method/basis set	$^{2}A'' \rightarrow {}^{1}A'$	³ A″	¹ A″	¹ A′	³ A″	ΔE_{S-T}^{b}
CCSD/aug-cc-pVDZ	2.773	3.278		2.536	2.489	-0.047
CCSD/aug-cc-pVTZ	2.792	3.254		2.575	2.512	-0.063
$CCSD(T)/aug-cc-pVTZ^{c}$	2.721	3.331		2.551	2.631	0.080
EOM-IP-CCSD/aug-cc-pVD ^{c,d}	2.739	3.245				
EOM-IP-CCSD/aug-cc-pVTZ ^{c,d}	2.924	3.442				
EOM-IP-CCSD(dT)/aug-cc-pVDZ ^{c,d}	2.575	3.121				
EOM-IP-CCSD(dT)/aug-cc-pVTZ ^{c,d}	2.738	3.306				
EOM-SF-CCSD/aug-cc-pVDZ ^{c,d,e}			4.688 ^f			0.0015
EOM-SF-CCSD/aug-cc-pVTZ ^{c,d,e}			4.828 ^f			-0.052
EOM-SF-CCSD(dT)/aug-cc-pVDZ ^{c,d,e}			4.241 ^f			0.052
EOM-SF-CCSD(dT)/aug-cc-pVTZ ^{c,d,e}			4.313 ^f			0.010
experiment	2.76(5)	3.25(5)		~2.5		

^{*a*}All values are given in electronvolts, without zero-point energy corrections. The experimental VDE values, determined in this work, are included for comparison. ^{*b*}Negative sign of ΔE_{S-T} indicates that the triplet state lies adiabatically below the singlet, and vise versa. ^{*c*}From single-point calculations carried out for CCSD/aug-cc-pVTZ optimized geometries of the anion and the neutral states (as appropriate), summarized in Figure 5. ^{*d*}B3LYP orbitals were used as the basis for single-point coupled-cluster calculations to reduce the effect of spin-contamination (see the text for details). ^{*e*}Calculations were performed starting from the high-spin ($M_S = 1$) reference, whereas the singlet–triplet splitting was determined for the low-spin ($M_S = 0$) component of the triplet state, as recommended by the authors of spin-flip.^{30,47} *f*Calculated as the EOM-SF excitation energy of the ¹A" state (the leading two-determinant configuration shown in Figure 5) relative to the ³A" ($M_S = 1$) reference, combined with the VDE of the ²A" \rightarrow ³A" ($M_S = 1$) detachment transition determined using the corresponding EOM-IP method.

bonding orbital of a carbene anion (the triplet channel) to yield a predominantly parallel PAD. In the photodetachment from the π orbital (the singlet channel), a predominantly perpendicular PAD is expected.⁵ Thus, given resolved singlet and triplet bands, photoelectron imaging of carbenes allows the assignment of the transitions (and hence the ground-state multiplicity of the carbene), based on qualitative examination of raw photoelectron images.

4.2. CCICN⁻ Band Assignments. A similar analysis is now applied to CClCN. The spectrum in Figure 4b consists of two main overlapping features, which we expect to correspond to the lowest-energy singlet and triplet states of CClCN. These states are ${}^{1}A'$, ... $(15a')^{2}(4a'')^{0}$, and ${}^{3}A''$, ... $(15a')^{1}(4a'')^{1}$, where 15a' and 4a'' are CClCN's canonical σ and π carbene orbitals. Although the band separation in Figure 4b is not as good as in the CCl₂ case (Figure 4a), it is good enough to see that the outer (lower-eBE) band in the CClCN⁻ image has a slightly perpendicular PAD, whereas the more intense higher-eBE transition comes with a clearly parallel angular distribution. On the basis of these qualitative PADs, following the arguments laid out in section 4.1, we assign the lower-eBE band to the closed-shell singlet state of CCICN (¹A'), and the higher-eBE transition is assigned to the triplet state $({}^{3}A'')$. As an aside, a similar analysis could not be applied in the dicyanocarbene case, because the overlap of the singlet and triplet bands in the $C(CN)_2^-$ photoelectron image made it impossible to resolve even the qualitative character of the corresponding PADs.¹⁵

Figure 4b also reveals a possible additional transition, appearing as a weak central spot in the image and distinguishable as a shoulder (marked *) near the spectral cutoff. If indeed distinct from the ${}^{3}A''$ band, this transition could correspond to the open-shell singlet state ${}^{1}A''$, ... $(15a')^{1}(4a'')^{1}$. The plausibility of this assignment is argued in section 4.6.

The photoelectron spectrum in Figure 4b has been modeled as a sum of three bands: a simple Gaussian for ${}^{1}A'$ and modified Gaussians (eq 1) for the ${}^{3}A''$ and (*) bands, which are close to

the energetic cutoff. The resulting fit to the experimental spectrum is shown in Figure 4b. From the fit, the VDE corresponding to the ¹A' band is 2.76 ± 0.05 eV, with an onset of the transition observed around 2.5 eV. The VDE corresponding to the ³A'' state is 3.25 ± 0.05 eV. These results are included in Table 3.

4.3. Anion and Neutral Geometries. Ab initio calculations were performed for the anion and the singlet and triplet states of the neutral carbene. The geometries were optimized²⁶ at the CCSD level of theory with the aug-cc-pVTZ basis set. The resulting structures of the ²A" ground state of the anion and the closed-shell singlet (¹A') and the triplet (³A") states of the neutral are shown in Figure 5. All three equilibrium structures are planar but differ in detail, particularly the bond angle at the carbene center. The anion geometry is closest to that of the singlet, with a small difference in the bond angle, but a notable change in the C–Cl bond length. The triplet structure has a more open carbene bond angle, with a 30° difference with respect to the anion. The optimized geometry of the open-shell singlet, ¹A", is not included in the figure but is expected to be most similar to the ³A" geometry.

On the basis of these structures, we expect a broad Franck– Condon envelope for the triplet band, more so than the singlet. Thus, although the experimental VDE of the triplet is ~0.5 eV higher than that of the singlet (Figure 4b), the difference in the adiabatic electron affinities (equal to the singlet–triplet splitting, $\Delta E_{\rm S-T}$) is expected to be significantly smaller, i.e., $\Delta E_{\rm S-T} < 0.5$ eV. The origin of the triplet band is not observed in Figure 4b, not only due to the overlap with the singlet but also possibly because of a small Franck–Condon factor corresponding to the 0–0 transition. Hence, the EA of the triplet carbene and $\Delta E_{\rm S-T}$ cannot be estimated on the basis of the experimental results alone. A higher-resolution spectrum with detailed Franck–Condon modeling would be helpful.¹¹ From the available data, no definite conclusion can be drawn even about the *sign* of the singlet–triplet splitting.⁴⁶



Figure 5. Manifolds of the low-lying electronic states of neutral CCICN, calculated using the EOM-SF-CCSD(dT)/aug-cc-pVTZ method for the equilibrium geometries of the anion, the singlet neutral, and the triplet neutral. The geometries were optimized at the CCSD/aug-cc-pVTZ level of theory. The bond lengths are shown in angstroms. For each of the three geometries, the vertical ordering of the ${}^{1}A'$, ${}^{3}A''$ ($M_{S} = 0$), and ${}^{1}A''$ states is indicated, with the energies given relative to the lowest state *at that geometry*. Two energy values are given for each of the target states: the EOM-SF-CCSD results (in plain font) and those including the noniterative diagonal triples corrections (dT) (in bold). The dominant electron configurations for each of the target states are also indicated, with the orbitals shown corresponding to the two nonbonding carbene orbitals, $15a'(\sigma)$ and $4a''(\pi)$.

4.4. Electron Affinity and Vertical Detachment Energy. The adiabatic EAs of the ${}^{1}A'$ and ${}^{3}A''$ states of the CClCN carbene, as well as the corresponding anion VDEs were computed²⁶ using the coupled-cluster theory. In addition to full geometry optimizations at the CCSD level, single-point CCSD(T)/aug-cc-pVTZ calculations were carried out²⁶ for the CCSD/aug-cc-pVTZ optimized geometries. The VDEs were also computed³² directly using the EOM-IP-CCSD(dT) method, using the above anion geometry. The results are summarized in Table 3.

The calculated VDE values, corresponding to detachment to both the ¹A' and ³A" states, are in good agreement with the peak energies in the experimental spectrum (Figure 4b). In particular, we note the excellent agreement of the CCSD/augcc-pVTZ results with the experiment (2.792 and 3.254 eV vs 2.76 ± 0.05 eV and 3.25 ± 0.05 eV for the ¹A' and ³A" VDEs, respectively). Inclusion of the triple excitations, CCSD(T), does not improve the predictions, possibly because the triples are included without the corresponding geometry relaxation. A good agreement with the experimental values is also observed for the EOM-IP-CCSD(dT)/aug-cc-pVTZ results (2.738 and 3.306 eV vs the above experimental VDEs). With the EOM-IP-CCSD method, inclusion of the diagonal triples correction (dT)³¹ lowers the VDE values, whereas increasing the basis set size from double to triple- ζ has an opposite effect.

The calculated EA values for the closed-shell singlet carbene (Table 3) also agree very well with the observed onset of the ${}^{1}A'$ band in Figure 4.

4.5. Singlet–Triplet Splitting of Chlorocyanocarbene. Per section 4.4, at the relaxed geometry of the anion, singlet CCICN is expected to lie (vertically) ~0.5 eV lower than the triplet. This prediction is in excellent agreement with the experimental results in Figure 4b, where the ¹A' band peaks 0.5 eV below the ³A" band maximum. The calculations further predict that the relaxed geometry of the singlet is more similar to that of the anion than to the triplet state's structure (Figure 5). Accounting for the geometry relaxation, the singlet and the triplet states of CCICN are nearly degenerate, with a very small adiabatic energy gap. The CCSD/aug-cc-pVTZ calculations (Table 3) predict a slightly negative $\Delta E_{S-T} = -0.063$ eV (i.e., the triplet is below the singlet), whereas inclusion of the triples correction, CCSD(T), results in a positive $\Delta E_{S-T} = 0.080$ eV (the triplet higher than the singlet).⁴⁶

The above predictions were obtained within a singlereference formalism. Taking into account the multiconfigurational nature of cyanocarbenes, we adopt a more appropriate description, based on the spin-flip method.^{27–30} Although also rooted in a nominally single-reference formalism, the EOM-SF strategy allows us to calculate the energies of the low-spin excited states starting from a robust high-spin reference, thus providing a more accurate description of the multiconfigurational target states.³⁰ We use the high-spin ($M_{\rm S} = 1$) component of the ³A" state of CClCN as a reference to describe the closed- and open-shell singlet states, ¹A' and ¹A", as well as the low-spin ($M_{\rm S} = 0$) component of the ³A" state itself. All target states are described with single spin-flip excitations of the reference, as apparent from their leading electron configura-tions included in Figure 5.

The SF calculations were carried out³² with the aug-cc-pVTZ basis set for each of the three CCICN geometries shown in Figure 5, corresponding to the CCSD/aug-cc-pVTZ optimized structures of the anion, the closed-shell singlet, and the triplet. As the use of HF orbitals indicated significant spin contamination in the wave functions, unrestricted B3LYP orbitals were used for the EOM-SF-CCSD calculations, taking advantage of the relative insensitivity of coupled-cluster theory to the choice of orbital bases. Typical spin expectation values $\langle S^2 \rangle = 2.02-2.04$ were achieved for the triplet reference, compared to the 2.25-2.35 range resulting from the unrestricted HF orbitals. As recommended by Krylov,⁴⁷ the energy of the $M_{\rm S} = 0$ component of the ³A" state, rather than that of the $M_{\rm S} = 1$ reference, was used for calculating the singlet-triplet energy gaps.

The results are summarized in Figure 5. For each of the three geometries studied, the vertical ordering of the ${}^{1}A'$, ${}^{3}A''(M_{S}=0)$, and ¹A" states is indicated, with the energies given relative to the lowest state at that geometry. Two energy values are given for each of the target states: the EOM-SF-CCSD results (in plain font) and those including the noniterative diagonal triples corrections $(dT)^{31}$ (in bold). The dominant electron configurations for each of the target states are also indicated, with the orbitals shown corresponding to the two nonbonding carbene orbitals, 15a' (σ) and 4a" (π). The open-shell target states, i.e., the open-shell singlet, ${}^{1}A''$, and the $M_{S} = 0$ component of the triplet, ³A", are described as linear combinations of the two dominant configurations shown. As always, the symmetric (with respect to exchange) spin combination corresponds to the triplet state, and the antisymmetric corresponds to the open-shell singlet.

The findings for the anion geometry can be compared directly to the experimental results. The photoelectron spectrum from Figure 4b is reproduced on the left margin of Figure 5, with the bands aligned to coincide approximately with the corresponding neutral states. Both the experiment and theory show that at this geometry the ¹A' state of CCICN is lower in energy than the ³A'' state. The experimentally determined difference between the two VDEs (0.49 \pm 0.07 eV, per Table 3) is in agreement with the vertical singlet—triplet gap predicted by the calculations. We find again (as in section 4.4) the EOM-SF-CCSD result (0.47 eV) to agree slightly better with the experiment than that including the triples correction (0.59 eV), but both values fall within or very close to the uncertainty range.

By comparison of the absolute energies of the target states at different geometries, the adiabatic relaxation energy of the closed-shell ¹A' state relative to the anion geometry and the adiabatic singlet—triplet splitting of the carbene are determined (Figure 5 and Table 3). With the highest-level/largest basis set used EOM-SF-CCSD(dT)/aug-cc-pVTZ method, we obtain $\Delta E_{\rm S-T} = 0.010$ eV. This estimate is small in magnitude, consistent with the CCSD(T)/aug-cc-pVTZ results. The

positive sign of ΔE_{S-T} implies that the singlet, ¹A', is the ground state of the carbene.

Though these conclusions are consistent with the experimental spectrum, the predicted magnitude of ΔE_{S-T} is so small that, for practical purposes, the singlet and triplet states should be viewed as nearly degenerate. This is especially true, considering how far apart these states are in the configuration space.

4.6. Open-Shell Singlet of CCICN. The results in Figure 5 also shed light on the plausibility of assigning the weak nearzero-eKE feature (*) in Figure 4b to the open-shell singlet state of CCICN. The VDE of the ${}^{2}A'' \rightarrow {}^{1}A''$ transition was calculated as the VDE of ${}^{2}A'' \rightarrow {}^{3}A''$, determined by the EOM-IP-CCSD method, combined with the EOM-SF-CCSD excitation energy of the ${}^{1}A''$ state relative to the ${}^{3}A''$ ($M_{\rm S} = 1$) reference. The results are included in Table 3. Although the predicted VDE > 4 eV is significantly above the 3.5 eV photon energy, the ${}^{2}A'' \rightarrow {}^{1}A''$ transition is expected to have a broad Franck–Condon envelope, similar to the ${}^{2}A'' \rightarrow {}^{3}A''$ band in Figure 4b, as follows from the common orbital components, ... $(15a')^{1}(4a'')^{1}$, of the ${}^{3}A''$ and ${}^{1}A''$ wave functions.

The results in Table 3 and Figure 5 suggest that even at the ${}^{3}A''$ geometry the ${}^{1}A''$ carbene lies at or just above ~3.5 eV (obtained as the adiabatic EA of the high-spin component of the ${}^{3}A''$ state combined with the EOM-SF excitation energy of ${}^{1}A''$ relative to the triplet reference). Full geometry relaxation of the ${}^{1}A''$ state will lower the energy further and hence we expect adiabatic EA(${}^{1}A''$) \leq 3.5 eV. Therefore, it is indeed possible that the weak band (*) in the proximity of the energetic cutoff in Figure 4 is due to the open-shell carbene. Future experiments at higher photon energy may clarify this assignment.

5. SUMMARY AND CONCLUSIONS

5.1. Results Summary. The observed VDE of CHClCN⁻, 2.39 \pm 0.04 eV, is in excellent agreement with the CCSD(T)/

Table 4. Ground-State Multiplicity and the Singlet-Triplet Splitting (eV) of Halo- and Cyanocarbenes^a

carbene	singlet/triplet	$\Delta E_{ m S-T}/ m eV$	ref		
CH_2	triplet	-0.390 ± 0.004	5		
Halocarbenes					
CHF	singlet	0.646 ± 0.017	48		
CHCl	singlet	0.18 ± 0.11	48		
CCl_2	singlet	0.9 ± 0.2	11		
Cyanocarbenes					
HCCN	triplet	-0.516 ± 0.017	14		
$C(CN)_2$	triplet	-0.52 ± 0.05	15		
Chlorocyanocarbene					
CClCN	(singlet) ^b	~0.01 ^c	this work		

^{*a*}Positive ΔE_{S-T} values correspond to the singlet ground states. ^{*b*}The parentheses indicate that the experiment is inconclusive with regard to the ground-state multiplicity of CCICN, whereas the most advanced theory methods predict a singlet ground state. However, the predicted singlet-triplet splitting is small enough that the singlet and triplet states, separated significantly in the configuration space, should be viewed as effectively degenerate. ^{*c*}Theory estimate, consistent with the experimental results.

aug-cc-pVTZ prediction of 2.40 eV. The significant geometry change predicted for the detachment transition (nonplanar pyramidal anion \rightarrow trigonal planar neutral) is consistent with the broad photoelectron band observed in the experiment. The



Figure 6. Relative ordering of the singlet (S) and triplet (T) states of $CCl_{2\nu}^{11}$ CClCN, and $C(CN)_{2\nu}^{15}$ with the corresponding EAs, adiabatic singlet-triplet splittings (ΔE_{S-T}), and approximate carbene bond angles in both the neutral and the anion (A) states shown.

adiabatic EA of the chlorocyanomethyl radical is determined as 1.86 ± 0.08 eV. This result is the first determination of the EA using spectroscopic data.

From the above EA(CHClCN) and the acidity/affinity cycle, the C–H BDE of chloroacetonitrile is determined, $DH_{298}(H-CHClCN) = 87.0 \pm 2.7$ kcal/mol. The corresponding radical stabilization energy (due to the mixed Cl and CN substitution) is 17.9 \pm 2.7 kcal/mol.

Photoelectron imaging of CClCN⁻ reveals two main transitions, assigned to the closed-shell singlet (¹A') and the triplet (³A") states of the CClCN carbene. The respective VDEs are 2.76 ± 0.05 and 3.25 ± 0.05 eV. A hint of the low-energy tail of a third, higher-energy band is present in the data, tentatively assigned to the open-shell singlet (¹A") state of the carbene. The experimental results are in good agreement with the theoretically predicted singlet—triplet vertical energy gap at the anion geometry, but inconclusive with regard to the adiabatic state ordering and the magnitude of the singlet—triplet splitting in CClCN. Ab initio calculations, using the spin-flip approach in combination with the coupled-cluster theory, predict that the ¹A' and ³A" states are near-degenerate adiabatically, with the ¹A' state just below ³A" ($\Delta E_{S-T} \approx 0.01$ eV).

5.2. Cl vs CN Substitution Effects. The EAs of substituted radicals and carbenes increase with the Cl and/or CN substitution, commensurate with the substituents' electronegativity. More intricate effects are observed in the intramolecular charge distributions and the relative energies of the radical and carbene π orbitals.

One important observation concerns the structure of the CHClCN⁻ anion. To put it in perspective, most substituted methylides, including $CHCl_2^{-,11}$ exhibit similar pyramidal structural motifs. To the contrary, $CH(CN)_2^{-}$ is planar, as is the corresponding radical, $CH(CN)_2^{.43}$ The planar geometry is attributed to the strong electron-withdrawing properties of the cyano-substituent, as even in the anion, the central carbon atom in $CH(CN)_2^{-}$ is positively charged.⁴³

With the drastically different geometries of $CHCl_2^-$ and $CH(CN)_2^-$, the structure of the mixed anion, $CHClCN^-$, is not obvious à priori, but the results presented here indicate that $CHClCN^-$ is similar to $CHCl_2^-$, rather than $CH(CN)_2^-$. It too has a nonplanar equilibrium geometry, with a negative charge on the central carbon (Figure 3). For further insight, consider that the singly substituted anion $NCCH_2^-$ is also nonplanar, in contrast to $CH(CN)_2^{-.42,43}$ Substituting a π -donor Cl for one of the hydrogens in $NCCH_2^-$ pushes the resulting anion toward $CHCl_2^-$, reinforcing the nonplanar bonding motif with a negative charge on the central carbon. Thus, among the doubly substituted methylides, the structural properties of $CHClCN^-$ are similar to those of $CHCl_2^-$, rather than $CH(CN)_2^-$.

An opposite trend is seen in the stabilities of the corresponding radicals, determined by the substituent effects on their singly occupied π HOMOs. As determined in this work, CHClCN is significantly more stable than CHCl₂ but is similar in this regard to CH(CN)₂. The Cl substituent is thus more effective in stabilizing a doubly substituted radical when accompanied by CN, rather than a second Cl.

Moreover, the effect of the heterogeneous CN and Cl substitution is similar to, and may even be greater than, the sum of the respective first substitutions, as seen by comparing RSE(CH₂ClCN) to RSE(CH₃Cl) + RSE(CH₃CN) (Table 2). This is remarkable, because substitution effects are generally not additive, with the incremental effect of the second substituent usually smaller than that of the first. This is clearly borne out, for example, by the RSE values for CH_{4-n}Cl_n and CH_{4-n}(CN)_n in Table 2. The results of this work suggest cooperative (captodative) interaction of Cl and CN, whereas the unsaturated π resonance (due to CN) combined with the π donation (due to Cl) yields a mixed doubly substituted radical of increased stability.

The effects of substitution on the ground-state multiplicity and the singlet-triplet splitting in the halo- and cyanocarbenes are summarized in Table 4.^{5,11,14,15,48,49} For CCl₂, CClCN, and $C(CN)_2$, the relative ordering of the singlet and triplet states (which is related to, but not the same as, the ordering of the spectral bands in Figure 4) is shown schematically in Figure 6.^{11,15} Unlike the corresponding radicals and their anions, chlorocyanocarbene does not resemble either dichlorocarbene¹¹ or dicyanocarbene.¹⁵ Instead, the mixed species is intermediate between the two homogeneously substituted carbenes. In CCl₂, π donation by the halogen atoms destabilizes the nonbonding $2p(\pi)$ orbital on the carbene center, thus favoring the $...\sigma^2 \pi^0$ configuration and a singlet ground state.³ In C(CN)2,11 the CN substituent has an opposite effect, stabilizing the π orbital via resonance interaction, so that the ... $\sigma^{1}\pi^{1}$ configuration and a triplet ground state are favored.^{3,15} In CClCN, the π donation by the halogen, on the one hand, and π resonance stabilization by CN, on the other, result in a neardegeneracy of the $...\sigma^2 \pi^0$ and $...\sigma^1 \pi^1$ configurations and the respective singlet and triplet states.

Other properties of the mixed CCICN carbene are also intermediate between its homogeneously substituted analogues. First, as shown in Figure 6, the respective electron affinities increase from CCl₂ to CCICN to C(CN)₂, as expected due to a combination of the inductive and π resonance properties of CN. Second, a similar trend is exhibited by the carbene bond angles. In all three systems in Figure 6, the carbene bond angle of the anion (A) is similar to that of the closed-shell singlet carbene (S), whereas the bond angle in the triplet (T), as well as in the open-shell $\sigma^1 \pi^1$ singlet (not shown), is much more open. This trend is understood in terms of the electronic structure properties of carbenes³ and the triplet-state bond angle in CCICN falls between the respective triplets of CCl₂ and C(CN)₂.

In conclusion, the π -donor halogen and π -acceptor cyano groups exhibit a cooperative effect on the stability of the heterogeneously substituted radical and, to the contrary, competing effects on the singlet-triplet splitting in the mixed carbene.

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ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (grant CHE-1011895).

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