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Halocarbenes CHF, CHCl, and CHBr: Geometries, Singlet–Triplet Separations, and Vibrational Frequencies

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Abstract: The fluorocarbene, chlorocarbene, and bromocarbene molecules in their lowest singlet and triplet electronic states have been studied via ab initio quantum mechanical methods. Basis sets of triple-ζ-plus double polarization quality were used in conjunction with self-consistent-field (SCF), two-configuration (TC) SCF, and configuration interaction (CI) methods. All three molecules have singlet ground states, with the singlet–triplet separations predicted to be 13.2 kcal (CHF), 5.4 kcal (CHCl), and 4.1 kcal (CHBr). Vibrational frequencies, infrared intensities, molecular structures, and dipole moments are predicted for the lowest singlet and triplet electronic states of all three molecules.

After the prototype methylene (CH_2) molecule, the simplest well-known carbenes are the monohalocarbenes CHF, CHCl, and CHBr. These molecules have been of interest to organic and physical chemists for some time, as a study of several review volumes will show.[1-5] Many of the studies of these halocarbenes have been directed at a determination, direct or indirect, of the energy difference between the lowest singlet and triplet electronic states. By their constitution, the monohalocarbenes should have properties intermediate between those of the prototype CH_2 (triplet ground state 9.1 kcal/mol below the lowest singlet state)[6-8] and the dihalocarbenes CF_2, CCl_2, and CBr_2. Although there are no precise experimental values of ΔE(S–T) for the latter three molecules, experiment[1-4] and theory[9,10] concur that all three have singlet ground states.

Theoretical estimates of the singlet–triplet separations ΔE(S–T) for the dihalocarbenes are 49 kcal (CF_2), 17 kcal (CCl_2), and 11 kcal (CBr_2).[9,10] By comparison with the CH_2 value ΔE(S–T) = −9.1 kcal, one senses the possibility that among the monohalocarbenes, CHCl and especially CHBr are possible candidates for triplet ground states. As noted by Moss and Jones[4] in their 1981 review, "halocarbenes have been regarded as archetypal singlets". In light of the Bauschlicher study[9] of 1977, however, Moss and Jones concluded that CHCl and CHBr might have low-lying triplet states. Bauschlicher and co-workers predicted ΔE(S–T) = 1.6 kcal for chlorocarbene and ΔE(S–T) = −1.1 kcal for bromocarbene. However, Moss and Jones[4] note wisely that even if CHBr, for example, had a triplet ground state, its chemistry might still be singlet carbene chemistry, since "most of these carbenes are born in the singlet state. If the rate of reaction of the singlet is much greater that that of the triplet, it may well be that singlet reactions are all that will be observed regardless of the ground state of the molecule".

The electronic spectra ($\tilde{X}\ {}^1A' \rightarrow \tilde{A}\ {}^1A''$ transitions) of CHF and CHCl have been known for some time[11,12] and are in fact discussed in Herzberg's classic 1967 monograph.[13] However, much more recently, there has been a wave of interest[14-22] in the high-resolution spectroscopy of CHF and one important similar paper[23] on CHCl. As a result of these new experiments, there now exist reliable molecular structures[18,23] for both CHF and CHCl, high-resolution values[21] of ν_2 for the $\tilde{X}\ {}^1A'$ and $\tilde{A}\ {}^1A''$ states of CHF, and electric dipole moments[19] for both singlet states of CHF.

There were two primary motivations for the present theoretical study of CHF, CHCl, and CHBr. First, in light of the availability of new spectroscopic information primarily for CHF, we predict here the lowest singlet- and triplet-state vibrational frequencies for all three molecules. Second, we are now in a position to make much more reliable predictions of the singlet–triplet separations of the three molecules than were Bauschlicher et al. (BSB)[9] in 1977. Hopefully, this theoretical study will stimulate continued experimental interest in the monohalocarbenes.

Theoretical Approach

The earlier research of Bauschlicher and co-workers[9] was carried out using double-ζ (DZ) basis sets augmented by a singlet set of d functions on the carbon atom. For CHF and CHCl, the carbon d function orbital exponents α were optimized for both singlet and triplet carbenes. For fluorocarbene, the optimum orbital exponents were $\alpha = 0.66$ (singlet) and $\alpha = 0.61$ (triplet). Similarly for chlorocarbene, the d function orbital exponents were 0.49 (singlet) and 0.46 (triplet). For bromocarbene, the singlet and triplet orbital exponents were both estimated to be $\alpha = 0.40$. The triplet carbene electronic states were described by single-configuration self-consistent-field (SCF) wave functions, while the singlet carbenes were described within the two-configuration (TC) SCF approximation.

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In the present research, it was decided to significantly increase the size of basis set used by BSB.[9] Generally speaking, the basis sets used in the present research were of triple-ζ-plus double polarization (TZ+2P), or slightly higher, quality. These basis sets are explicitly given in Table I. The hydrogen, carbon, and fluorine basis sets are taken from Dunning's contractions[24] of Huzinaga's primitive Gaussian sets.[25] A scale factor of $(1.2)^2 = 1.44$ was applied to the Gaussian orbital exponents of the hydrogen (5s/3s) basis set. The carbon atom polarization functions (α = 1.5 and 0.35) span the range of optimum single orbital exponents for CHF, CHCl, and CHBr.

The chlorine basis set is Dunning's (7s6p) contraction[26] of Veillard's (12s9p) primitive Gaussian set.[27] Like the carbon and fluorine bases, the chlorine set is of triple-ζ quality in the valence s space and quadruple-ζ calibre in the valence p space. Consistent with recent polarization function suggestions,[28] the two sets of chlorine orbital exponents were taken as α = 1.5 and 0.35.

Our bromine atom basis set is based on the unpublished primitive Gaussian basis and contraction scheme of Dunning.[29] We began with the (9s7p2d) contraction of Dunning's (14s11p5d) set. However, it was appreciated that this Br basis set may be deficient in the valence region. Therefore, using the "even-tempered" criterion of Ruedenberg and coworkers,[30] we added more spatially diffuse functions to the original Dunning set.[29] Specifically, one s function (α = 0.066), one p function (α = 0.046), and two sets of d functions (α = 0.54 and 0.19) were appended and yield the final Br basis, designated Br(15s12p7d/10s8p4d). It is important to note that the last two sets of d functions (α = 0.54 and 0.19) are in fact polarization functions, the other two sets of Br 3d orbitals being used essentially exclusively for the description of the Br atom 3d orbital. Thus the Br basis matches that for the other atoms, namely H, C, F, and Cl. We shall see that the additional Br basis functions significantly effect the predicted structures of singlet and triplet CHBr.

In the spirit of the BSB paper,[9] we began with SCF predictions of the structure of the triplet halocarbenes and TCSCF predictions of the singlet equilibrium geometry. At these levels of theory, the vibrational frequencies were predicted within the harmonic approximation using analytic-energy second-derivative methods.[31,32]

Orbital energies for the three triplet halocarbenes are given in Table II. A knowledge of the electron configurations of the three species CHF, CHCl, and CHBr allows us to understand the configuration interaction (CI) treatments undertaken for the different species. There are 12 valence electrons for each of the three molecules. For the triplet states all single and double excitations (CISD) with respect to the single SCF reference configuration were included. For the singlet halocarbenes, our zeroth-order descriptions are the TCSCF wavefunctions given in eq 1–3.

$$\Phi(\mathrm{CHF}) = c_1 ... 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 + c_2 ... 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 2a''^2 \quad (1)$$

$$\Phi(\mathrm{CHCl}) = c_1 ... 6a'^2 7a'^2 8a'^2 2a''^2 9a'^2 10a'^2 + c_2 ... 6a'^2 7a'^2 8a'^2 2a''^2 9a'^2 3a''^2 \quad (2)$$

$$\Phi(\mathrm{CHBr}) = c_1 ... 12a'^2 13a'^2 14a'^2 5a''^2 15a'^2 16a'^2 + c_2 ... 12a'^2 13a'^2 14a'^2 5a''^2 15a'^2 6a''^2 \quad (3)$$

Our standard configuration interaction (CI) treatment in this research was to hold doubly occupied the core orbitals in all configurations. For CHF these are the 1a′ (F 1s) and 2a′ (C 1s) orbitals. With this restriction, the CI included all single and double excitations having the nonzero Hamiltonian matrix element[33,34] with the reference configuration(s). For the lowest $^3A''$ state of CHF, this amounts to 42 465 configurations. When the singlet state of CHF is described by one configuration [the first configuration in (1)], the CI includes 34 234 configurations. When all single and double excitations with respect to both TCSCF reference configurations are included, the total configurations is 65 347. For fluorocarbene only the CI's were also carried with no orbitals frozen, and the numbers of configurations are 73 851 (triplet), 61 869 (one-reference singlet), and 119 604 (two-reference singlet).

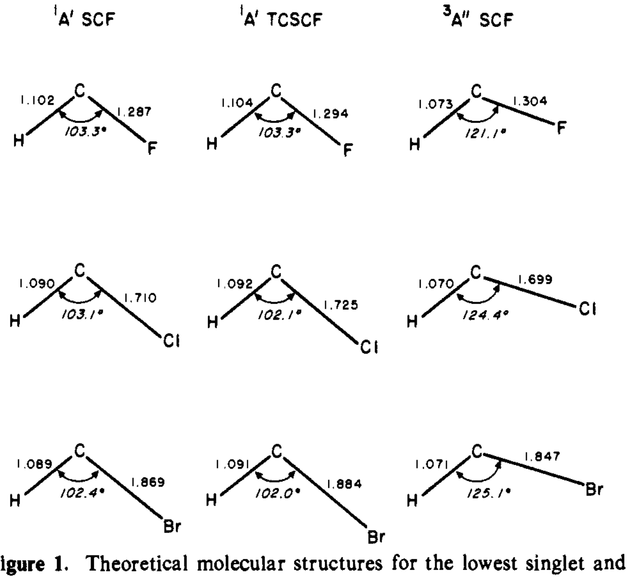

Figure 1. Theoretical molecular structures for the lowest singlet and triplet electronic states of the monohalocarbenes CHF, CHCl, and CHBr. All bond distances are given in angstroms.

For chlorocarbene (CHCl), there are 12 core electrons (1s, 2s, $2p_x$, $2p_y$, $2p_z$ chlorine and 1s carbon) and these are held doubly occupied in all configurations. All virtual orbitals were included in the CISD procedure, yielding totals of 48 368 (triplet), 39 070 (one-reference singlet), and 74 546 (two-reference singlet) configurations.

Finally, for bromocarbene, there was the additional question of whether to freeze the MOs corresponding to the bromine 3d atomic orbitals. Table II shows that these five orbitals have a narrow range of orbital energies, −3.197 to −3.211 hartrees. Nevertheless, it was decided to include these five molecular orbitals in the CI procedure. Therefore, for CHBr a total of 10 (1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$ Br and 1s C) molecular orbitals were held doubly occupied in all configurations. In addition the 10 counterpart virtual orbitals were deleted from the CI procedure. In this manner, the CISD approach yielded totals of 155 796 (triplet), 133 146 (one-reference singlet), and 261 714 (two-reference singlet) configurations.

Results

Fluorocarbene, CHF. The present theoretical predictions for CHF are summarized in Tables III and VI and Figure 1. The TCSCF structure (Figure 1) predicted for CHF is qualitatively similar to that of BSB.[9] However, the larger basis set used here does result in a decrease in the predicted bond distances. In particular the C–F distance r_e is 1.294 Å, 0.031 Å less than BSB's prediction. The present prediction is 0.011 Å less than the experimental vibrationally averaged r_0(C–F) = 1.305 ± 0.006 Å result of Suzuki et al.[18] Correlation effects are expected to increase this C–F bond distance[35] and could be expected to ultimately provide close agreement with experiment. Our r_e(C–H) is 1.104 Å, or 0.007 Å less than BSB's theoretical prediction with a smaller basis set. We are somewhat hesitant concerning the experimental value of the Hirota group, r_0(C–H) = 1.138 ± 0.010 Å. It would be surprising to find the TZ+2P TCSCF level of theory in error by 0.034 Å for a C–H bond distance. The C–H distance in CHF appears to be one property for which theory does better than experiment at the present time. Our H–C–F bond angle of 103.3° agrees satisfactorily with Hirota's experimental 104.1°.

The structure of triplet CHF is not known, since no spectroscopic transitions have yet been assigned to the $^3A''$ state. There are, however, hints in the 1984 paper by Suzuki et al.[20] that such analysis may be forthcoming. These authors[20] state that "perturbations (have been) ascribed to (a) low-lying triplet, but no quantitative analysis has been feasible". For $^3A''$ CHF, we did use the CISD method (73 851 configurations; see previous section) to predict a correlated geometrical structure, and this is

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Table I. Basis Sets of Contracted Gaussian Functions for the Theoretical Study of Halocarbenes

H (5s 2p/3s 2p)			C (10s 6p 2d/5s 4p 2d)			F (10s 6p 2d/5s 4p 2d)		
type	orbital exponent	contractn coeff	type	orbital exponent	contractn coeff	type	orbital exponent	contractn coeff
s	48.4416	0.025374	s	9471.0	0.000776	s	23340	0.00057
s	7.28352	0.189681	s	1398.0	0.006218	s	3431.0	0.006081
s	1.65168	0.852921	s	307.5	0.033575	s	757.7	0.032636
			s	84.54	0.134278	s	209.2	0.131704
s	0.462384	1.0	s	26.91	0.393668	s	66.73	0.396240
s	0.145872	1.0	s	9.409	0.544169	s	23.37	0.543672
			s	9.409	0.248075	s	23.37	0.264893
p	1.4	1.0	s	3.500	0.782844	s	8.624	0.767925
p	0.25	1.0						
			s	1.068	1.0	s	2.692	1.0
			s	0.4002	1.0	s	1.009	1.0
			s	0.1351	1.0	s	0.3312	1.0
			p	25.37	0.038802	p	65.66	0.037012
			p	5.776	0.243118	p	15.22	0.243943
			p	1.787	0.810162	p	4.788	0.808302
			p	0.6577	1.0	p	1.732	1.0
			p	0.2480	1.0	p	0.6206	1.0
			p	0.09106	1.0	p	0.2070	1.0
			d	1.5	1.0	d	1.5	1.0
			d	0.35	1.0	d	0.35	1.0

Cl (12s 9p 2d/7s 6p 2d)			Br (15s 12p 7d/10s 8p 4d)		
type	orbital exponent	contractn coeff	type	orbital exponent	contractn coeff
s	105747.0	0.001520	s	439700.0	0.000813
s	15855.3	0.011958	s	66030.0	0.006285
s	3615.32	0.061818	s	15140.0	0.031923
s	1030.03	0.245448	s	4317.0	0.128794
s	339.691	0.755094	s	1414.0	0.394591
			s	523.9	0.541292
s	124.497	1.0			
			s	523.9	0.183066
s	49.5143	0.702223	s	207.7	0.617646
s	20.8138	0.326653			
			s	85.54	1.0
s	6.46497	1.0	s	30.52	1.0
s	2.52567	1.0	s	12.98	1.0
s	0.53814	1.0	s	4.412	1.0
s	0.19356	1.0	s	1.862	1.0
			s	0.5455	1.0
p	587.622	0.007907	s	0.1902	1.0
p	139.745	0.061593	s	0.0660	1.0
p	44.790	0.274775			
p	16.5885	0.749524			
p	6.60076	1.0	p	2957.0	0.022262
p	2.71409	1.0	p	700.3	0.180188
p	0.95008	1.0	p	224.6	0.862405
p	0.35827	1.0			
p	0.12499	1.0	p	82.59	0.343999
			p	33.19	0.507099
			p	14.20	0.258957
d	1.5	1.0	p	14.20	0.079647
d	0.35	1.0	p	7.438	0.373442
			p	3.526	1.0
			p	1.595	1.0
			p	0.4918	1.0
			p	0.1507	1.0
			p	0.0460	1.0
			d	134.8	0.014827
			d	35.39	0.109328
			d	12.16	0.345060
			d	4.341	0.489355
			d	1.535	1.0
			d	0.540	1.0
			d	0.190	1.0

Table II. Orbital Energies (in hartrees) for the Lowest Triplet States of the Halocarbenes, within the Ordinary Single-Configuration SCF Approximation. The Core Electrons of the Halogen Atoms Are Identified in Parentheses[a]

CHF			CHCl			CHBr		
						1a′	−490.0400	(1s)
						2a′	−65.1774	(2s)
						3a′	−58.5353	(2p)
						4a′	−58.5338	
						1a″	−58.5338	
						5a′	−11.3080	(3s)
						6a′	−9.8585	
						7a′	−7.4710	
						8a′	−7.4632	(3p)
			1a′	−104.8567	(1s)	2a″	−7.4630	
			2a′	−11.3091		9a′	−3.2108	(3d)
			3a′	−10.5822	(2s)	10a′	−3.2068	
			4a′	−8.0507	(2p)	3a″	−3.2067	
1a′	−26.3265	(1s)	5a′	−8.0478		4a″	−3.1974	
2a′	−11.3234		1a″	−8.0477		11a′	−3.1974	
3a′	−1.6516		6a′	−1.1513		12a′	−1.0703	
4a′	−0.8927		7a′	−0.8272		13a′	−0.8182	
5a′	−0.7354		8a′	−0.6064		14a′	−0.5725	
1a″	−0.7053		2a″	−0.5018		5a″	−0.4550	
6a′	−0.6694		9a′	−0.4938		15a′	−0.4493	
7a′	−0.5249*		10a′	−0.5056*		16a′	−0.5028*	
2a″	−0.4045*		3a″	−0.4117*		6a″	−0.4175*	

[a] * = singly occupied molecular orbital.

Table III. Total Energies (in hartrees) and Relative Energies (in kcal/mol) for Fluorocarbene, HCF

method	optimized struct	tot energies		rel energies	
		$^{1}A'$	$^{3}A''$	$^{1}A'$	$^{3}A''$
SCF	SCF	−137.81397	−137.82009	0.0	−3.8
TCSCF/SCF	TCSCF/SCF	−137.83580	−137.82009	0.0	9.9
CI	SCF	−138.15212	−138.13804	0.0	8.8
previous entry	Davidson corrected	−138.18006	−138.16108	0.0	11.9
CI[a]	CI[a]		−138.18486		
CI[a]	SCF	−138.19792	−138.18479	0.0	8.2
previous entry	Davidson corrected	−138.22871	−138.21058	0.0	11.4
two-ref CI/CI	TCSCF/SCF	−138.15865	−138.13804	0.0	12.9
previous entry	Davidson corrected	−138.18279	−138.16108	0.0	13.6
two-ref CI/CI[a]	TCSCF/SCF	−138.20474	−138.18479	0.0	12.5
previous entry	Davidson corrected	−138.23165	−138.21058	0.0	13.2

[a] All SCF occupied and virtual orbitals included in CI.

Table IV. Total Energies (in hartrees) and Relative Energies (in kcal/mol) for Chlorocarbene, HCCl

method	optimized struct	tot energies		rel energies	
		$^{1}A'$	$^{3}A''$	$^{1}A'$	$^{3}A''$
SCF	SCF	−497.84527	−497.86298	0.0	−11.1
TCSCF/SCF	TCSCF/SCF	−497.86631	−497.86298	0.0	+2.1
CI	SCF	−498.13119	−498.12975	0.0	+0.7
previous entry	Davidson corrected	−498.16194	−498.15569	0.0	+3.9
two-ref CI/CI	TCSCF/SCF	−498.13712	−498.12975	0.0	+3.7
previous entry	Davidson corrected	−498.16435	−498.15569	0.0	+5.4

given in Figure 1. The figure shows that the effects of electron correlation on the structure are minor and predictable.[35] The C–H distance increases by 0.004 Å, the C–F distance increases by 0.007 Å, and the H–C–F bond angle increases by 0.5°. These results support our suggestion that the experimental C–H distance for singlet CHF is too long.

The basis sets used in this research are sufficiently large to suggest that we are approaching the Hartree-Fock limit for energy differences. Therefore our prediction of ΔE(S–T) = −3.8 kcal for CHF at the SCF level of theory should be close to the Hartree–Fock value. Thus CHF is predicted to have a triplet ground state in single-configuration Hartree–Fock theory. However, when the singlet state is described by a TCSCF wave function, it becomes the ground state, lying 9.9 kcal below the triplet. As discussed by BSB and elsewhere[36–40] in some detail, it is well-established that this use of single-configuration SCF wave function for the triplet carbene in conjuction with a TCSCF wave function for the singlet carbene gives a reasonable rendering of the singlet–triplet separation. For CH_2 with a large basis set, for example, the TCSCF/SCF energy difference is 10.9 kcal/mol,[40] to be compared with experiment,[6–8] 9.1 kcal/mol.

After the first two lines, the remainder of Table III deals with explicitly correlated wave functions. Taken as a whole, these suggest that the TCSCF singlet/SCF triplet approximation for CHF is not quite as good as shown[7,40] for the prototype carbene CH_2. Our most reliable prediction of ΔE(S–T) is 13.2 kcal/mol, 3.3 kcal greater than the TCSCF/SCF prediction. The 13.2-kcal prediction was obtained by applying the Davidson correction (for quadrupole excitations, specifically unlinked clusters)[41,42] to the singlet two-reference CI/triplet one-reference CI energies. We suggest a reliability of roughly ±2 kcal for this 13.2-kcal prediction. BSB[9] predicted that singlet CHF lies 9.2 kcal below the lowest triplet state. Finally, it should be noted that the explicit treatment of correlation for the core electrons (see Table III) reduces ΔE(S–T) by about 0.5 kcal/mol.

The discussion of CHF is completed by reference to the vibrational frequencies seen in Table VI. Also included in this table are infrared intensities. If past experience is a reliable guide,[43,44] the TZ+P SCF and TCSCF harmonic vibrational frequencies should be about 10% greater than the true fundamentals. Such a scaling yields for TCSCF singlet CHF ν(C–H stretch) = 2715 cm^{-1}, ν(C–F stretch) = 1155 cm^{-1}, and ν(bend) = 1384 cm^{-1}. Of these three vibrational frequencies, only the bending mode has been characterized experimentally. In 1966, Merer and Travis[11] reported ν_2 = 1403 cm^{-1}, while much more recently Hakuta[21] reports ν_2 = 1406.9 cm^{-1}. Our theoretical estimates agree satisfactorily (to within 19 and 23 cm^{-1}, respectively) with both experimental values for ν_2(CHF).

It is also of interest to compare the vibrational frequencies from theory with the matrix-isolated IR spectrum of Jacox and Milligan.[45] The failure of Jacox and Milligan to observe the bending frequency of CHF in the IR is completely consistent with the very weak IR intensity (0.2 km/mol) predicted in Table VI. Jacox and Milligan assign an absorption at 1182 cm^{-1} to CHF and suggest (see Table VII of their paper[45]) that it may correspond to the C–F stretching frequency. This assignment is consistent with our prediction ν(C–F stretch) = 1155 cm^{-1}, when sources of error in both approaches are considered. Jacox and Milligan speculate that one of the unassigned bands at 2918 and 3262 cm^{-1} might be due to the C–H stretch in CHF. Our estimated ν(C–H stretch) = 2715 cm^{-1} would appear to rule out either possibility.

The triplet CHF vibrational frequencies are quite different from the above-discussed singlet results. Specifically the C–H stretch

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Table V. Total Energies (in hartrees) and Relative Energies (in kcal/mol) for Bromocarbene, HCBr

method	optimized struct	tot energies $^1A'$	tot energies $^3A''$	rel energies $^1A'$	rel energies $^3A''$
SCF	SCF	−2610.70431	−2610.72432	0.0	−12.6
TCSCF/SCF	TCSCF/SCF	−2610.72546	−2610.72432	0.0	0.7
CI	SCF	−2611.09097	−2611.09264	0.0	−1.0
previous entry	Davidson corrected	−2611.13039	−2611.12674	0.0	2.3
two-ref CI/CI	TCSCF/SCF	−2611.09760	−2611.09264	0.0	3.1
previous entry	Davidson corrected	−2611.13323	−2611.12674	0.0	4.1

Table VI. Harmonic Vibrational Frequencies (cm^{-1}) Predicted for the Halocarbene Molecules HCX. Infrared Intensities (in km/mol) Are Given in Parentheses

	HCF	HCCl	HCBr
	$^1A'$ SCF		
C–H stretch	3027 (1.222)	3160 (0.372)	3178 (0.207)
C–X stretch	1304 (2.130)	812 (1.262)	691 (0.907)
bend	1546 (0.255)	1309 (0.066)	1244 (0.047)
μ, D	1.58	1.58	
	$^1A'$ TCSCF		
C–H stretch	3017 (1.294)	3145 (0.424)	3164 (0.247)
C–X stretch	1283 (2.193)	797 (1.301)	679 (0.912)
bend	1538 (0.199)	1309 (0.039)	1244 (0.027)
μ, D	1.44	1.44	1.39
	$^3A''$ SCF		
C–H stretch	3332 (0.076)	3362 (0.067)	3359 (0.061)
C–X stretch	1338 (1.221)	869 (0.501)	753 (0.240)
bend	1240 (0.479)	1089 (0.012)	1031 (0.024)
μ, D	1.32	1.15	1.13

of the triplet is about 10% higher and the order of the C–F stretch and bending frequencies is reversed relative to the singlet state. Moveover, the infrared intensities are quite different between these two electronic states. Specifically, the C–H stretch intensity is substantial for singlet CHF but very weak for triplet CHF.

Chlorocarbene, CHCl. The theoretical predictions of this work for CHCl are summarized in Tables IV and VI and Figure 1. The predicted TCSCF singlet C–Cl bond distance, r_e = 1.725 Å, is decreased by 0.037 Å relative to BSB's work.[9] However, this distance is still too long compared to Merer and Travis's 1966 spectroscopic value[12] of 1.68_9 Å. Our TCSCF prediction is also long compared to Kakimoto et al.'s 1983 spectroscopic conclusions,[23] r_0(C–Cl) = 1.687 ± 0.011 Å and r_z(C–Cl) = 1.696 ± 0.003 Å. Our TCSCF r_e(C–H) = 1.092 Å is 0.009 Å shorter than BSB's prediction with their smaller basis. Here comparison with Hirota's experiments[23] is not entirely meaningful in light of their large error bars, i.e., r_0(C–H) = 1.130 ± 0.036 Å. Our predicted bond angle θ_e(HCCl) = 102.1° falls within Hirota's error bars for both θ_0 = 105.1 ± 4.7° and r_z = 101.4 ± 1.2°. Merer and Travis[12] reported θ = 103.4° for the H–C–Cl bond angle.

Although there is no experimental structure for triplet CHCl, the increased bond angle (by 22.3°) relative to the lowest singlet state is typical of other carbenes. In the prototype CH_2 this difference is 134°–103° = 31°, even greater than for CHCl. The C–Cl distance for the triplet state is 0.026 Å shorter than for the analogous singlet, a result in the opposite direction of that predicted for CHF. However, like CHF, CHCl is predicted to have a shorter C–H distance in its triplet state than for the analogous singlet. The C–Cl and C–H bond distances are 0.036 and 0.005 Å, respectively, shorter than the earlier predictions of BSB.

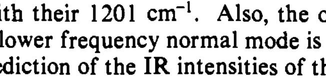
The predicted energetics of CHCl are shown in Table IV. With our basis set, which should provide SCF energetics close to the Hartree–Fock limit, triplet CHCl lies 11.1 kcal/mol below the lowest singlet state when both states are described by single-configuration SCF wave functions. The TCSCF singlet–SCF triplet value for ΔE(S–T) is 2.1 kcal; i.e., the singlet state lies lower energetically. This prediction is very close to the analogous 1.6 kcal obtained by BSB with their smaller basis set. However, as with CHF, the higher levels of theory, allowing for the explicit introduction of electron correlation, favor the singlet state relative to the triplet. Thus ΔE(S–T) for CHCl is increased to 3.7 kcal at the two-reference CI singlet/one-reference CI triplet level of comparison. Our final prediction of 5.4 kcal for the singlet–triplet energy difference is provided by appending Davidson corrections[41,42] to the 3.7 kcal CI result. Including estimated error bars, our predicted singlet–triplet energy gap is 5.4 ± 2 kcal/mol, or 3.8 kcal higher than that of BSB.[9]

Harmonic vibrational frequencies and infrared intensities for chlorocarbene are included in Table VI. For singlet CHCl, the SCF and TCSCF predictions are quite comparable. As discussed above, we may estimate the true fundamentals by multiplying the TCSCF harmonic frequencies by 0.9. This procedure yields ν(C–H stretch) = 2831 cm^{-1}, ν(C–Cl stretch) = 717 cm^{-1}, and ν(bend) = 1178 cm^{-1}. To our knowledge, there are no experimental gas-phase vibrational frequencies with which to compare these predictions.

However, Jacox and Milligan[46] have observed the IR spectrum of CHCl in argon and nitrogen matrices. From these spectroscopic experiments, they conclude that ν(C–Cl stretch) ≅ 805–815 cm^{-1} and ν(bend) = 1201 cm^{-1}. Our theoretical C–Cl stretch (717 cm^{-1}) is somewhat lower than the matrix isolation value of 805–815 cm^{-1}, but our bending frequency (1178 cm^{-1}) agrees satisfactorily with their 1201 cm^{-1}. Also, the observed higher intensity of the lower frequency normal mode is consistent with our ab initio prediction of the IR intensities of these two fundamentals.

Bromocarbene, CHBr. The present theoretical predictions for CHBr are given in Tables V and VI and Figure 1. For singlet CHBr, one sees in Figure 1 a major structural shift compared to the predictions of BSB. For example, in the TCSCF singlet structure, r_e(C–Br) = 1.884 Å, a full 0.088 Å less than predicted by BSB. For triplet CHBr, we predict r_e(C–Br) = 1.847 Å, less by 0.044 Å than BSB. One must conclude that the expansion of the basis set here relative to BSB yields large and nonuniform bond distance shortenings. This result is primarily due to the presence of the two sets of d-type polarization functions in the present basis set (Table I). Clearly these additional basis functions are important for precise molecular structure predictions for molecules containing bromine.

There is no experimental structural or spectroscopic information available at present for CHBr. However, it is reasonable to cite the "normal" C–Br bond distance in methyl bromide, CH_3Br. That distance[48] is r(C–Br) = 1.938 Å, a value 0.054 Å longer than our singlet CHBr prediction and 0.091 Å longer than our triplet CHBr prediction. This ordering, of course, is quite reasonable since C=X double bond resonance structures such as



(4)

have long been invoked for halocarbenes.[47] The latter closed-shell valence structure, of course, only applies to singlet CHBr.

Total and relative energies for singlet and triplet CHBr are seen in Table V. These results are readily harmonized with the generally accepted view that singlet carbenes are preferentially stabilized (relative to the analogous triplet states) by electronegative substituents. Specifically since Br is the least electronegative[9,49]

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of the series F, Cl, and Br, CHBr is expected to have the smallest ΔE(S–T), assuming the singlet carbene is in each case the ground state. The same results may be understood in terms of the π-donor abilities[50–52] of the substituents F, Cl, and Br.

At the SCF level of theory, triplet CHBr is incorrectly predicted to be the ground state, lying 12.6 kcal below the lowest singlet state. However, when the TCSCF description (3) is used for the singlet state, the latter falls lower in energy, but by only 0.7 kcal. Higher levels of theory further preferentially stabilize singlet CHBr, leading ultimately to a 4.1-kcal value for ΔE(S–T). This result differs by 5.2 kcal from the BSB prediction[9] that triplet CHBr lies 1.1 kcal below the lowest singlet state. Including estimated error bars, our predicted singlet–triplet energy difference is 4.1 ± 2 kcal.

Vibrational frequency and IR intensity predictions for bromocarbene are given in Table VI. Reducing the TCSCF frequencies by 10% for ground-state singlet CHBr yields 2848 cm^{-1} (C–H stretch), 611 cm^{-1} (C–Br stretch), and 1120 cm^{-1} (bending). Since triplet CHBr is predicted to lie only 4.1 kcal higher, it is not inconceivable that its infrared spectrum might be observed in the not-too-distant future. Singlet and triplet CHBr should in principle be distinguishable by the prediction that the triplet C–H stretching frequency lies 176 cm^{-1} higher, at 3023 cm^{-1}. The problem is that the IR intensity of the C–H stretch for all three triplet monohalocarbenes is rather low, less than 0.1 km/mol. For both singlet and triplet states of all three molecules, the carbon–halogen stretching frequency is predicted to be the most intense among the three fundamentals.

Some Concluding Comparisons

The theoretical predictions reported here are for the most part consistent with what is known experimentally about the carbenes CHF, CHCl, and CHBr. Exceptions are the CH distances in singlet CHF and (perhaps) CHCl and the C–H stretching frequency of fluorocarbene. In addition, we provide predictions of many properties of these molecules not yet observed in the laboratory. Most notably there is apparently no spectroscopic observation to date of CHBr. The remainder of this concluding section is devoted to comparisons between the three carbenes.

The dipole moments of the three molecules are predicted in Table VI and that of singlet CH_2 at a comparable level of theory is reported elsewhere.[53] For the lowest singlet states, the predicted TZ+2P TCSCF dipole moments are −1.66 (CH_2), 1.44 (CHF), 1.44 (CHCl), and 1.39 (CHBr) D. The halocarbene dipole moments are essentially equal and show little dependence on halogen atom electronegativity. The predicted triplet-state dipole moments from TZ+2P SCF theory are −0.59 (CH_2), 1.32 (CHF), 1.15 (CHCl), and 1.13 (CHBr).

The only experimental information concerning halocarbene dipole moments comes from the paper by Dixon and Wright.[19] For the $\tilde{X}\,^1A'$ ground state of CHF, they find $\mu_a = 0.061 \pm 0.005$ D, where μ_a is the dipole moment along the a rotational axis. Dixon and Wright also suggest that the dipole moment component μ_b could also be quite large ($\approx$1 D). For singlet CHF, the present TCSCF theory predicts $\mu_a = 0.36$ and $\mu_b = 1.40$ D.

Errors of this magnitude (0.3 D) for dipole moments are not unusual at the Hartree–Fock level of theory.[54] Therefore, it was decided to evaluate the dipole moment using the configuration interaction (CISD) method. The results, $\mu_a = 0.066$ and $\mu_b = 1.424$ D, are in essentially perfect agreement with the experimental μ_a value of Dixon and Wright.[19]

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Note Added in Proof. D. G. Leopold and W. C. Lineberger informed us on April 8 that they have experimentally determined an upper limit of 15 kcal/mol for the singlet–triplet energy separation for CHF. This is consistent with the present theoretical prediction of 13.2 kcal/mol.

Registry No. CHF, 13453-52-6; CHCl, 2108-20-5; CHBr, 17141-28-5.

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Mechanism of the Thermal [1,5]-H Shift in *cis*-1,3-Pentadiene. Kinetic Isotope Effect and Vibrationally Assisted Tunneling

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Abstract: Ab initio 3-21G calculations have been performed for the [1,5]-H shift in *cis*-1,3-pentadiene. A transition state of C_s symmetry has been compared with one of C_{2v} symmetry. The lowest energy configuration of this latter structure has B_1 symmetry and must therefore be described by an open-shell calculation. The energy of this structure is favored by 5.2 kcal/mol over the one of C_s symmetry. Both structures are found to be real transition states. Both the calculated reaction rates and the kinetic isotope effects are found to be considerably smaller than the observed ones. A mechanism is suggested in which tunneling takes place between high-vibrational states of the reactant and the product. It is shown that this mechanism is most likely for the transition state of C_{2v} symmetry. The calculated tunneling rates indicate that the [1,5]-H shift in *cis*-1,3-pentadiene mainly takes place via this mechanism.

The thermal [1,5]-H shift in *cis*-1,3-pentadiene is an example of the general class of sigmatropic reactions (Scheme I). In 1966, Roth and König[1] studied this reaction in the temperature range of 185–210 °C. They established an activation enthalpy of 35.4 kcal/mol and a kinetic isotope effect (KIE) for $k_H/k_D = 5.1$. The temperature dependence of the KIE was found to be $k_H/k_D = 1.15 \exp(1.4(\text{kcal/mol})/RT)$. From these observations they concluded that the reaction is a concerted process which proceeds through a symmetric pericyclic transition state (TS), thus confirming the predictions based on orbital symmetry considerations.

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