

loss of H· from **5** and **6** to give CH₂SH⁺ (**1**) are calculated to be of similar magnitude to that for the intramolecular rearrangement, hydrogen scrambling may occur upon loss of H· or D· from CD₃SH⁺.

(iv) In addition to the experimentally well-established dimethyl sulfide (**10**) and ethanethiol radical cations, the sulfonium ion CH₂SHCH₃⁺ (**11**) is likely to be an observable C₂H₆S⁺ isomer. This species is found to lie 82 kJ mol⁻¹ above CH₃SCH₃⁺, with a barrier to rearrangement to CH₃SCH₃⁺ of 120 kJ mol⁻¹. The barrier to dissociation of **11** to give CH₂SH⁺ and CH₃· is calculated to be 98 kJ mol⁻¹, with no reverse activation energy.

(v) The present results are consistent with the CH₂SH⁺ (**1**) ion rather than CH₃S⁺ (**2**) being formed by fragmentation of dimethyl sulfide at low ionizing energies. A two-step rearrangement-dissociation mechanism is found to lead to formation of CH₂SH⁺. This mechanism yields a barrier for the formation of CH₂SH⁺ from CH₃SCH₃⁺ which agrees well with that derived from the experimentally observed appearance energy for formation of CH₂SH⁺ from dimethyl sulfide.

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Overtone Spectral Investigation of Substituent-Induced Bond-Length Changes in Gas-Phase Fluorinated Benzenes and Their Correlation with ab Initio STO-3G and 4-21G Calculations

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Abstract: The gas-phase overtone spectra of eight fluorinated benzenes are measured in the CH-stretching regions corresponding to $\Delta v = 2$ to 5 and are analyzed in terms of the local mode model. Peaks corresponding to inequivalent CH bonds in monofluorobenzene and the three difluorobenzenes are partially resolved. The frequency shifts are compared to σ_1 , and the peaks are assigned to the various CH bonds on the basis of the substituent effect. CH bond lengths ($r_{\text{CH}}^{\text{LM}}$) are determined from the shift in the overtone peak frequency relative to benzene. These values are compared with bond lengths obtained from geometry-optimized ab initio molecular orbital calculations at the STO-3G ($r_{\text{CH}}^{\text{STO-3G}}$) and 4-21G ($r_{\text{CH}}^{\text{4-21G}}$) levels. There is excellent agreement between the values of $r_{\text{CH}}^{\text{LM}}$ and $r_{\text{CH}}^{\text{4-21G}}$. In fact, the local mode analysis would appear to provide the best available technique for determining CH bond lengths in molecules of this size. The redistribution of electron population upon substitution is examined in terms of a bond-strength parameter, which is derived from the Mulliken population analysis. This parameter correlates well with the calculated and experimental bond lengths and provides a simple physical interpretation of the observed variation in r_{CH} .

I. Introduction

The understanding of the effect of substituents on the properties of a parent molecule is of primary importance in the organization of chemical knowledge. In particular, studies on benzene and its substituted derivatives have formed a considerable area of research for many years. In an earlier paper,¹ we examined the higher CH-stretching overtones of 20 substituted benzenes in the liquid phase, using the local mode model.² A given CH bond behaves as an uncoupled anharmonic diatomic oscillator whose overtone transition energies are given by

$$\Delta E_{0 \rightarrow v} (\text{cm}^{-1}) = \omega v + Xv^2 \quad (1)$$

where ω is the local mode frequency, X is the diagonal local mode anharmonicity, and v is the CH-stretching vibrational quantum number. As ω is dependent on bond strength³ and X is sensitive to steric hindrance,⁴ unique CH bond types within a molecule can be spectrally resolved. In our liquid-phase study,¹ the lines were too broad to allow for resolution of inequivalent hydrogens, except in the case of nitrobenzene where a partially resolved doublet was observed. The assignment of the ortho hydrogens to the high-frequency peak was subsequently confirmed by partial deutera-

tion.⁵ We attempted to interpret the observed variation in the positions of the overtone frequencies of the substituted benzenes in terms of σ_1 , the inductive part of the Hammett σ , after the work of Katayama et al.^{6,7} The correlation of frequency shift with σ_1 was only moderately successful, and the effect clearly ceased to be additive at higher levels of substitution.

In the present work, we investigate the overtone spectra of a series of fluorinated benzenes in the gas phase. Preliminary results for 1,3-difluorobenzene have already been presented.⁸ Because of the decrease in intermolecular interactions in the gas phase, the overtone bands are narrower. Partially resolved peaks are observed corresponding to absorption from inequivalent CH bonds. This resolution leads to a greater understanding of the correlation of frequency shifts with σ_1 .

McKean and his collaborators have investigated the fundamental CH-stretching transitions in molecules where all the hydrogens but one have been replaced by deuterium.⁹ They have

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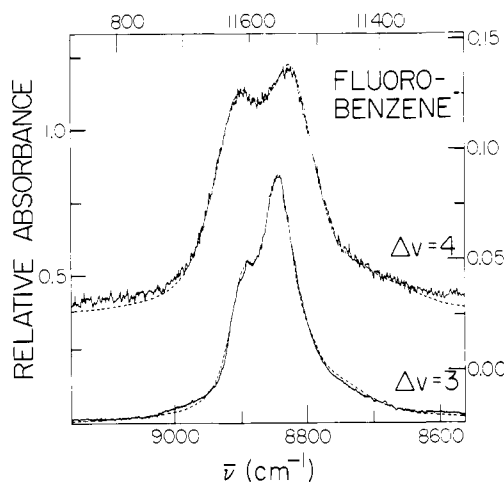


Figure 1. Calculated and experimentally observed overtone spectra of fluorobenzene in the regions of $\Delta v = 3$ (lower curve) and $\Delta v = 4$ (upper curve). The calculated band envelopes (dashed) represent the sum of Lorentzian peaks from a computer-assisted deconvolution of the experimentally observed overtone band. The experimental spectra were obtained in the gas phase at 86 °C.

observed an excellent correlation between this CH-stretching frequency, $\bar{\nu}_{\text{CH}}^{\text{iso}}$, and r_{CH} . Not surprisingly, similar correlations have been observed in the overtone spectra.¹⁰⁻¹² In the present work we investigate the correlation between overtone frequency shifts and values of r_{CH} determined from geometry-optimized ab initio molecular orbital calculations at the STO-3G¹³ and 4-21G¹⁴ levels. We extend this correlation to changes in the electron population distribution and attempt a simple physical interpretation of the results.

II. Experimental Section

All of the compounds were obtained commercially at 97+ to 99+% purity and used without further purification. The spectra were measured in the gas phase with a multiple path length gas cell (Wilks Scientific Corp., South Norwalk, Conn., Model 5720) equipped with a heating jacket. The temperature of the gas cell was kept constant at 86 °C. The procedure that was used for loading sample into the gas cell has been described elsewhere.¹⁵ The path length was varied, dependent on the molecule and the overtone, in the range 0.75–14.25 m. The spectra were recorded on a Beckman 5270 spectrophotometer with near-infrared and visible light sources. The digitized signal was transferred to a Nicolet 1280 computer. The data were converted to a linear energy scale, with data points at 1.22-cm⁻¹ intervals. At $\Delta v_{\text{CH}} = 4$ and 5, the absorption was often very weak so several spectra were recorded and signals averaged. In all cases, background spectra were recorded from the evacuated cell for each spectral scan and were subtracted from the sample spectra. Each spectrum was deconvoluted with a Nicolet curve analysis program which fitted Lorentzian peaks to the experimental data. The experimental and calculated spectra were plotted and compared to evaluate the quality of the deconvolution fit. The quality of the fit was also evaluated from the root-mean-square deviation.

Ab initio molecular orbital calculations with complete geometry optimization at the STO-3G level were performed for all the fluorobenzenes studied. The GAUSSIAN 70¹⁶ program or MONSTERGAUSS,¹⁷ which employs the force gradient method, was used. The results of a complete geometry optimization of benzene, fluorobenzene, 1,3-difluorobenzene, and 1,3,5-trifluorobenzene with the 4-21G split-valence basis set have been published.¹⁸ Using these geometries, we repeated the calculations with the MONSTERGAUSS 4-21G basis set. Changes in the electron population

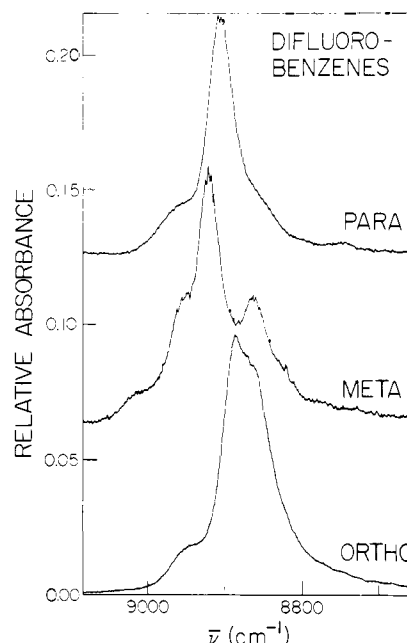


Figure 2. The overtone spectra of gas-phase 1,2-difluorobenzene (bottom), 1,3-difluorobenzene (middle), and 1,4-difluorobenzene (top) at 86 °C in the region of $\Delta v = 3$.

Table I. Deconvoluted Peak Positions and Local Mode Parameters

molecule	assignment	Δv	$\bar{\nu}$ (cm ⁻¹)	ω (cm ⁻¹)	X (cm ⁻¹)
fluorobenzene	H(2)	3	8 892	3140 ± 3	-58.6 ± 0.7
		4	11 617		
		5	14 234		
	H(3), H(4)	3	8 840	3127 ± 6	-60.3 ± 1.5
		4	11 535		
1,2-difluorobenzene	H(3)	3	8 889	3135 ± 1	-57.3 ± 0.3
		4	11 621		
		5	14 242		
	H(4)	3	8 859	3129 ± 4	-58.7 ± 1.0
		4	11 570		
1,3-difluorobenzene	H(2)	3	8 958	3160 ± 8	-57.5 ± 1.9
		4	11 727		
		5	14 355		
	H(4)	3	8 920	3150 ± 2	-58.8 ± 0.4
		4	11 661		
1,4-difluorobenzene	H(5)	3	8 863	3133 ± 8	-59.9 ± 2.0
		4	11 564		
		5	14 173		
	H(3)	3	8 904	3143 ± 6	-57.9 ± 1.4
		4	11 650		
1,3,5-trifluorobenzene	H(4)	3	8 980	3164 ± 8	-56.6 ± 2.0
		4	11 761		
		5	14 401		
1,2,3,4-tetrafluorobenzene	H(2)	2	6 076	3155 ± 3	-58.9 ± 1.0
		3	8 932		
		4	11 681		
1,2,3,5-tetrafluorobenzene	H(2)	2	6 108	3172 ± 3	-59.1 ± 0.9
		3	8 980		
		4	11 743		
1,2,4,5-tetrafluorobenzene	H(2)	2	6 089, 6 081 ^a	3159 ± 6	-57.6 ± 1.8
		3	8 964		
		4	11 709		

^a Line fit uses the center of the doublet at $\Delta v = 2$.

distribution with fluorine substitution were calculated from the Mulliken population analysis.

III. Results

Representative gas-phase overtone spectra of the eight fluorinated benzenes at $\Delta v = 2-5$ are shown in Figures 1-8. In Figure

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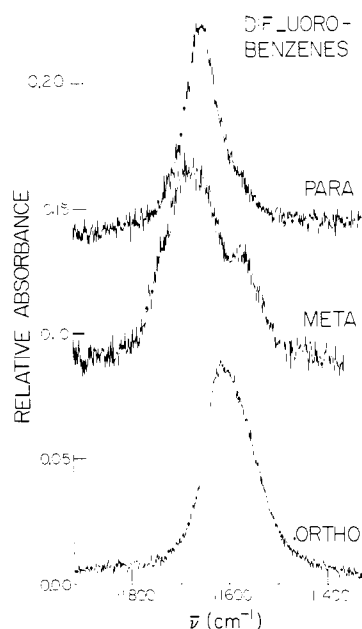


Figure 3. The overtone spectra of gas-phase 1,2-difluorobenzene (bottom), 1,3-difluorobenzene (middle), and 1,4-difluorobenzene (top) at 86 °C in the region of $\Delta\nu = 4$.

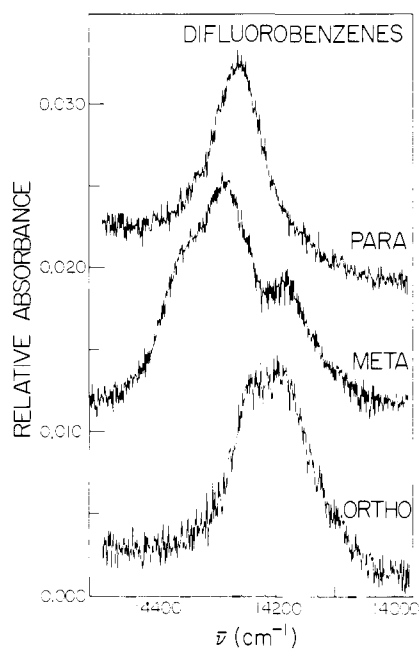


Figure 4. The overtone spectra of gas-phase 1,2-difluorobenzene (bottom), 1,3-difluorobenzene (middle), and 1,4-difluorobenzene (top) at 86 °C in the region of $\Delta\nu = 5$.

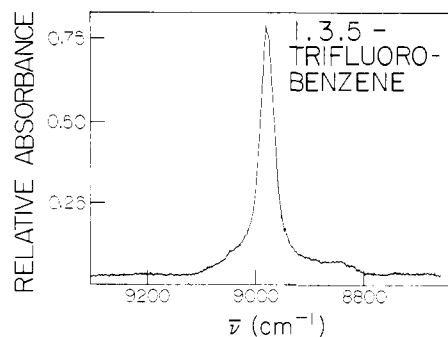


Figure 5. The overtone spectra of gas-phase 1,3,5-trifluorobenzene at 86 °C in the region of $\Delta\nu = 3$.

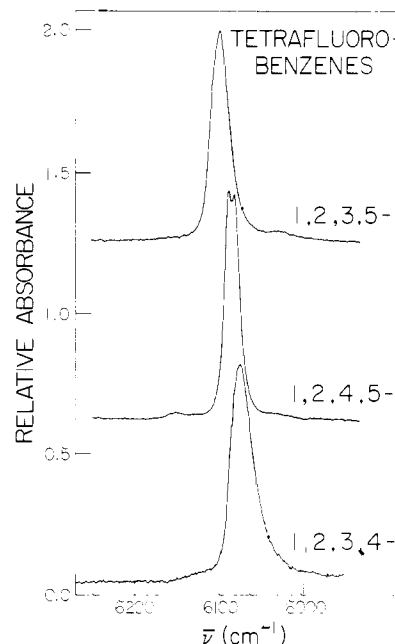


Figure 6. The overtone spectra of gas-phase 1,2,3,4-tetrafluorobenzene (bottom), 1,2,4,5-tetrafluorobenzene (middle), and 1,2,3,5-tetrafluorobenzene (top) at 86 °C in the region of $\Delta\nu = 2$.

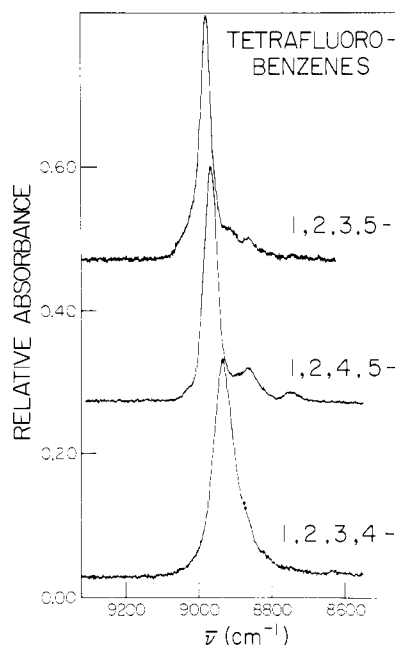


Figure 7. The overtone spectra of gas-phase 1,2,3,4-tetrafluorobenzene (bottom), 1,2,4,5-tetrafluorobenzene (middle), and 1,2,3,5-tetrafluorobenzene (top) at 86 °C in the region of $\Delta\nu = 3$.

1, the calculated spectra (dashed line) from the deconvolution program are included for $\Delta\nu = 3$ and 4 of fluorobenzene to illustrate the quality of the deconvolution fit. The positions of the partially resolved peaks, as determined by the deconvolution of each spectrum, are listed in Table I. The values were used in eq 1 to obtain the local mode parameters, ω and X , from a least-squares fit. These parameters are also given in Table I. The peaks were assigned to the various inequivalent CH bonds on the basis of frequency shift and correlation with the molecular orbital calculations (vide infra). The full widths at half maximum of the deconvoluted peaks are given in Table II.

The errors for the frequencies and anharmonicities in Table I are determined from the least-squares fitting procedure. They arise from uncertainties in the peak positions due to spectral breadth or to uncertainties in the deconvolution procedure. A third cause for such errors could be the presence of unresolved com-

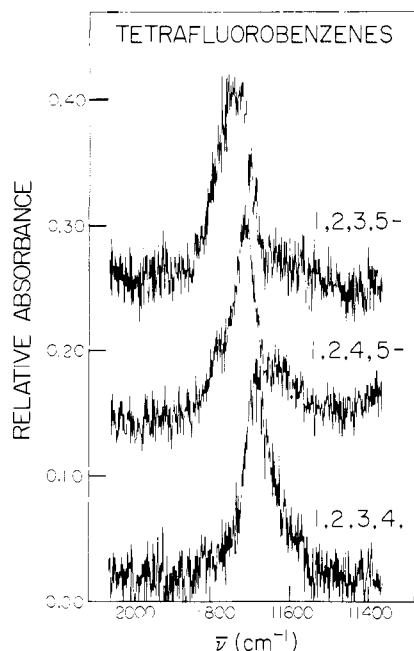


Figure 8. The overtone spectra of gas-phase 1,2,3,4-tetrafluorobenzene (bottom), 1,2,4,5-tetrafluorobenzene (middle), and 1,2,3,5-tetrafluorobenzene (top) at 86 °C in the region of $\Delta\nu = 4$.

Table II. Deconvoluted Gas-Phase Overtone Line Widths (cm^{-1}) of Fluorinated Benzenes

molecule	assignment	$\Delta\nu$			
		2	3	4	5
fluorobenzene	H(2)		52	89	103
	H(3), H(4)		54	85	121
1,2-difluorobenzene	H(3)	31	36	70	72
	H(4)		50	98	78
1,3-difluorobenzene	H(2)	31	42	87	67
	H(4)		34	92	91
1,4-difluorobenzene	H(5)	46	45	73	88
		13	39	80	101
1,3,5-trifluorobenzene		23	31	65	72
1,2,3,4-tetrafluorobenzene		31	63	81	
1,2,3,5-tetrafluorobenzene		26	35	100	
1,2,4,5-tetrafluorobenzene		11	40	66	
		11			

bination peaks. These peaks can contribute to the lower overtones and involve two quanta of a lower frequency normal mode. They lead to shifts in the overtone peak positions which result in deviations from the simple Birge Spomer relation (eq 1).

The uncertainties in the line widths depend primarily on three factors: the overtone ($\Delta\nu$), the noise level, and the presence and number of inequivalent CH bonds. Thus we estimate the uncertainties in the line widths for the five molecules with a single CH bond type to be $\leq 10\%$ (considerably $< 10\%$ for the lower overtones). For the other three molecules, we estimate the line-width uncertainties to be $\leq 20\%$, where the higher uncertainties are associated with the lower relative intensity peaks.

From their work on partially deuterated molecules, which was referred to in the Introduction, McKean and his collaborators have derived an empirical relationship between r_{CH} and the isolated fundamental CH-stretching frequency.⁹

$$r_{\text{CH}}^{\text{iso}} (\text{\AA}) = 1.3982 - 0.0001023 \bar{\nu}_{\text{CH}}^{\text{iso}} \quad (2)$$

Hayward and Henry¹⁰ reported a very good correlation between McKean's $\bar{\nu}_{\text{CH}}^{\text{iso}}$ and overtone CH-stretching frequencies at $\Delta\nu = 4$, $\bar{\nu}_{v=4}$. More recently, Mizugai and Katayama in their study of liquid-phase heterocyclics,¹¹ and Wong and Moore, in their

Table III. Frequency Shifts (cm^{-1}) Relative to Benzene^a at $\Delta\nu = 2$ to 5 for Fluorinated Benzenes in the Gas Phase

molecule	assignment	$\Delta\nu$			
		2	3	4	5
fluorobenzene	H(2)		94	119	128
	H(3), H(4)		42	37	48
1,2-difluorobenzene	H(3)		91	123	170
	H(4)		61	72	106
1,3-difluorobenzene	H(2)		160	229	282
	H(4)		122	163	207
1,4-difluorobenzene	H(5)		65	66	101
			106	152	188
1,3,5-trifluorobenzene			182	263	329
1,2,3,4-tetrafluorobenzene		104	134	183	
1,2,3,5-tetrafluorobenzene		135	182	245	
1,2,4,5-tetrafluorobenzene		117	166	211	

^a From ref 19.

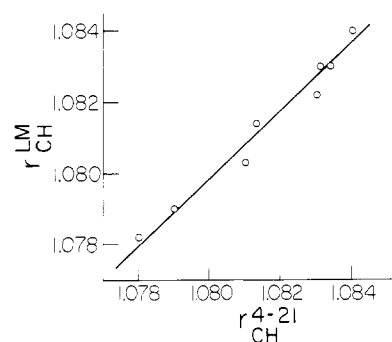


Figure 9. The correlation between CH bond lengths in fluorinated benzenes, which are obtained from frequency shifts in the overtone spectra, and CH bond lengths from ab initio molecular orbital calculations at the 4-21G level.¹⁸

study of the gas-phase alkanes,¹² have noted a correlation between overtone frequencies at $\Delta\nu = 6$ and CH bond lengths determined experimentally or from ab initio molecular orbital theories, respectively. In particular, Wong and Moore¹² obtained the relationship

$$r_{\text{CH}}^{4-31\text{G}} (\text{\AA}) = 1.319 \pm 0.022 - (1.426 \pm 0.134) \times 10^{-5} \bar{\nu}_{v=6} \quad (3)$$

where $r_{\text{CH}}^{4-31\text{G}}$ corresponds to CH bond lengths calculated from geometry-optimized molecular orbital calculations at the 4-31G level.

On the basis of eq 2 and 3, we used the relationship

$$r_{\text{CH}}^{\text{LM}} (\text{\AA}) = 1.084 - (\Delta\nu/11\nu)0.001 \quad (4)$$

to determine the CH bond lengths from the bond length in benzene, and the frequency shift relative to benzene, $\Delta\nu$. These frequency shifts were determined for each deconvoluted peak and are given in Table III. Bond lengths, which are obtained from the frequency shifts and eq 4, are averaged for the three overtones. CH bond lengths were also obtained by complete geometry optimization at the STO-3G level, $r_{\text{CH}}^{\text{STO-3G}}$, and for some molecules, from the literature values at the 4-21G level, $r_{\text{CH}}^{4-21\text{G}}$. The average values of $r_{\text{CH}}^{\text{LM}}$ are compared with the ab initio values in Table IV. The agreement between $r_{\text{CH}}^{\text{LM}}$ and $r_{\text{CH}}^{4-21\text{G}}$ is particularly good and this correlation is illustrated in Figure 9.

A measure of the change in the electron distribution with fluorine substitution, P^{basis} (vide infra), was determined from the Mulliken population analysis. The values of this parameter for both basis sets are also listed in Table IV. The correlation between

Table IV. Experimental and ab Initio CH Bond Lengths and Electron Population Parameters

molecule	assignment	$r_{\text{CH}}^{\text{LM}}$ (Å)	$r_{\text{CH}}^{\text{STO-3G}}$ (Å)	$r_{\text{CH}}^{\text{4-21G}^a}$ (Å)	$p_{\text{STO-3G}}$	$p_{\text{4-21G}}$
benzene		1.084	1.08258 ^b	1.084	4.963	5.547
fluorobenzene	CH(2)	1.0814	1.0819	1.0813	5.007	5.855
	CH(3)	1.0830	1.0825	1.0834	4.954	5.616
	CH(4)	1.0830	1.0821	1.0831	4.974	5.576
1,2-difluorobenzene	CH(3)	1.0811	1.0823		5.001	
	CH(4)	1.0822	1.0822		4.966	
1,3-difluorobenzene	CH(2)	1.0790	1.0809	1.079	5.054	6.170
	CH(4)	1.0803	1.0810	1.081	5.020	5.879
	CH(5)	1.0822	1.0835	1.083	4.946	5.684
1,4-difluorobenzene		1.0807	1.0823		4.973	6.190
1,3,5-trifluorobenzene		1.0782	1.0802	1.078	5.066	
1,2,3,4-tetrafluorobenzene		1.0797	1.0820		5.003	
1,2,3,5-tetrafluorobenzene		1.0782	1.0808		5.058	
1,2,4,5-tetrafluorobenzene		1.0790	1.0821		5.039	

^a From ref 18. ^b From ref 20.

Table V. Correlations among Bond Lengths and Electron Population Parameters

parameter A	parameter B	r
$r_{\text{CH}}^{\text{LM}^a}$	$r_{\text{CH}}^{\text{STO-3G}}$	0.792
$r_{\text{CH}}^{\text{LM}^a}$	$p_{\text{STO-3G}}$	-0.905
$r_{\text{CH}}^{\text{STO-3G}^a}$	$p_{\text{STO-3G}}$	-0.882
$r_{\text{CH}}^{\text{LM}^b}$	$r_{\text{CH}}^{\text{4-21G}}$	0.988
$r_{\text{CH}}^{\text{LM}^b}$	$p_{\text{4-21G}}$	-0.972
$r_{\text{CH}}^{\text{4-21G}^b}$	$p_{\text{4-21G}}$	-0.989

^a 14 data points. ^b 8 data points.

p_{basis} and $r_{\text{CH}}^{\text{LM}}$ is illustrated in Figure 10. The correlation coefficients for the various correlations which involve the bond lengths and parameters listed in Table IV were calculated and are given in Table V. The values of r , for which the probability of obtaining the same r value from random data is less than 0.001, are 0.78 for 14 data points and 0.92 for 8 data points.²¹

IV. Discussion

A. Local Mode Anharmonicity. The local mode parameters in Table I were determined from eq 1. The associated correlation coefficients are in the range from -0.9994 to -0.9999 which indicates an excellent linear fit. The magnitude of the diagonal local mode anharmonicity has been observed to decrease when steric hindrance restricts high amplitude CH vibrational motion.⁴ Because of the relatively small size of the fluorine substituent, such a change was not anticipated here. Indeed the value of X for all the bonds studied is very similar to that reported for gas-phase benzene ($-57.1 \pm 0.2 \text{ cm}^{-1}$).¹⁹ This constant value of X occurred even for CH bonds ortho to two fluorine atoms, as in 1,3,5-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, and 1,2,4,5-tetrafluorobenzene. In these molecules, X would also appear to be independent of substituent-induced changes in CH bond strength and the associated decrease in CH bond length.

B. ω , $\Delta\bar{\nu}$, and Peak Assignments. The value of ω varied with the degree of substitution and with the proximity of the CH bond to the substituent(s). In fact, the shift in overtone peak position was the most important factor in determining the peak assignment. In the spectrum of liquid nitrobenzene,¹ where inequivalent CH bonds give rise to a partially resolved doublet, the higher frequency peak was assigned to the two CH bonds ortho to the nitro group. This assignment was made for three reasons: the correlation between frequency shift and σ_1 , the area ratio of the two peaks, and the expectation that proximity to the nitro group would result in a greater decrease in r_{CH} and a greater shift of the CH-stretching peak to higher frequencies. This assignment was

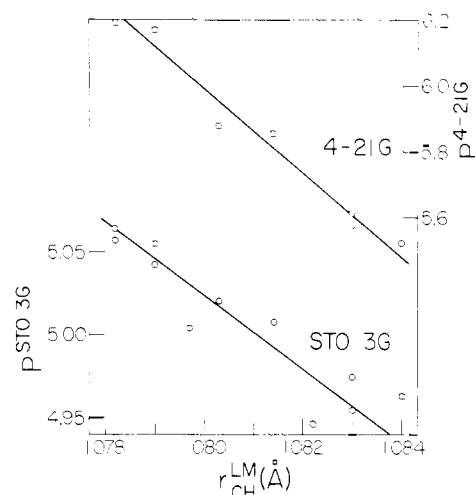


Figure 10. The correlation between CH bond lengths in fluorinated benzenes, which are obtained from frequency shifts in the overtone spectra, and a bond-strength parameter, which is derived from ab initio electron population analysis at the STO-3G level (bottom) or the 4-21G level (top).

subsequently confirmed by the spectra of the partially deuterated molecules.⁵

Like the nitro group, a fluorine substituent also exhibits σ electron-withdrawing properties, and therefore is expected to cause a decrease in aryl CH bond lengths relative to benzene. This decrease in r_{CH} would be expected to be greatest at the ortho position, and to be greater if more than one fluorine substituent were present on the ring. The overtone spectra of the fluorobenzenes that we have studied display precisely these characteristics. The CH-stretching frequencies of all the peaks are greater than those for the corresponding overtones in benzene (Table I). The spectra of fluorobenzene (Figure 1) consist of partially resolved doublets. The high-frequency peak is assigned to the two CH bonds ortho to the fluorine, the other to those meta and para to it. The spectra of the three difluorobenzenes (Figures 2, 3, and 4) are similar to the spectra of the three analogous xylenes,¹⁵ except that the fluorine substituents cause a shift to higher rather than lower frequencies. The 1,2-difluorobenzene spectra exhibit partially resolved doublets. The higher frequency peak is assigned to CH bonds in the 3 and 6 positions. The 1,3-difluorobenzene spectra exhibit triplet structure. The highest frequency peak is assigned to the CH bond in the 2 position, ortho to the two fluorines. The central frequency peak is assigned to the two equivalent CH bonds at positions 4 and 6, and the lowest frequency peak to the CH bond in position 5. In 1,4-difluorobenzene, 1,3,5-trifluorobenzene, and in the tetrafluorobenzenes, there is only a single CH bond type and only a single peak is observed in the spectra (Figures 5-8). Where inequivalent hydrogens exist, the ratios of the areas of the deconvoluted peaks are in accordance with the number of CH bonds assigned to them.

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Molecular orbital calculations at the STO-3G and 4-21G levels also predict a decrease in r_{CH} with increasing fluorine substitution. The correlation between the ab initio CH bond lengths and those calculated from eq 4 is good at the STO-3G level but improves significantly with the use of the larger split valence basis set (Table V).²² Factors governing the change in bond length are considered in the next section.

C. Correlation between $\Delta\nu$, Δr_{CH} , and Molecular Orbital Calculations. The CH bond lengths from the STO-3G calculations are close to those determined from the frequency shifts for the eight fluorobenzenes, but they do not model the small variations in $r_{\text{CH}}^{\text{LM}}$ very well. While the calculated $r_{\text{CH}}^{4-21\text{G}}$ values are less than the equilibrium CH bond lengths, the relative differences between bond lengths are expected to be quite accurate.¹⁸ In practice these values are scaled by the addition of a correction term.¹⁸ As we have noted, the correlation between $r_{\text{CH}}^{\text{LM}}$ and the corrected values of $r_{\text{CH}}^{4-21\text{G}}$ is excellent (Figure 9, Table V).

In order to understand the bond-length changes in terms of an electronic substituent effect, it is necessary to determine which factors change most upon substitution and correlate directly with the r_{CH} values. Molecular orbital calculations do not describe a molecule as possessing distinct chemical bonds. It is possible, by various mathematical techniques, to produce localized bond-like orbitals, but we have chosen to simply examine the electron distribution as determined by the population analysis matrix. The gross orbital population on an atom contains many contributing terms which involve overlap with the atomic orbitals on all other atoms in the molecule. In fact, the contribution of nonbonded electron population is generally small; e.g., for the hydrogen atom it is less than 10% of the gross population and varies only slightly upon substitution. For these reasons the nonbonded terms are omitted in our analysis.

Traditionally, bond orders have been defined in terms of orbital overlap.^{23,24} However, the importance of ionic contributions to bond strength have also been recognized in definitions of bond order.²⁴ Here we take a similar simplistic view of the CH bond. Thus we define a basis set dependent electron population parameter

$$P^{\text{basis}} = \sum_{\mu,\nu} P_{\mu\nu} S_{\mu\nu} - \sum_{\mu,\nu} P_{\mu\nu} S_{\mu\nu} + 2 \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \quad (5)$$

The covalent contribution to bonding is contained in the last term, which is simply a bond-order term and corresponds to the total electron population shared between the carbon and the hydrogen, i.e., twice the off-diagonal term between bonded carbon and hydrogen from the Mulliken population matrix condensed to atoms. Here μ and ν refer to atomic orbitals on carbon and hydrogen, respectively, and $P_{\mu\nu}$ and $S_{\mu\nu}$ have the usual significance of density matrix element and overlap integral.

The first two terms correspond to the electron population residing on carbon and hydrogen, respectively. These terms are given by the sum of the electron populations in each atomic orbital at a given center summed over all molecular orbitals, i.e., the diagonal terms in the Mulliken population matrix of charges condensed to atoms. In these terms, μ and ν are atomic orbitals either on carbon or on hydrogen as indicated by the superscript. The difference between the first two terms is a measure of the ionic contribution to bonding. We do not try to account for unequal sharing of electrons, although this would have a small additional effect.

Values of P^{basis} at the fully optimized geometries are given in Table IV, and the correlation coefficients for the correlations involving P^{basis} are given in Table V. Despite the number and type of approximations involved, the parameter correlates remarkably well with the changes in bond length. Although the value of P^{basis}

for a given CH bond varies considerably with the basis set, the same trend between different CH bonds is found at both the STO-3G and 4-21G levels. The correlation between P^{basis} and either $r_{\text{CH}}^{\text{LM}}$ or $r_{\text{CH}}^{\text{basis}}$ improves with the larger basis set.

The changes in electron distribution on fluorine substitution as described by the terms in P^{basis} are very nearly additive. For fluorobenzene these changes at the ortho, meta, and para positions in the σ and π electron populations for each carbon, the σ population for each hydrogen, and the covalent term can be evaluated. Then, on the basis of additivity, the total change for each CH bond in the di-, tri-, and tetrasubstituted molecules can be predicted. The results from such a simple additivity scheme are always within 2 to 3% of the values found from the calculation at the optimized geometry of the substituted molecule. At the STO-3G level, the quantity of σ electrons withdrawn and π electrons donated per fluorine remains almost constant at 0.200 electron withdrawn, and 0.070 electron donated per fluorine, even at tetrasubstitution. Comparable results are found in the 4-21G analysis. We found the amount withdrawn or donated decreased slightly when two or more fluorines were adjacent to each other on the ring. Presumably the competing factors result in a nonlinear response.²⁵

The reasons for the difficulties in the correlation of σ_1 and $\Delta\nu$ for the liquid phase are apparent from these gas-phase results. The presence of unresolved peaks due to inequivalent CH bonds is clearly responsible for the observed scatter in the liquid-phase correlation.¹ In particular, CH bonds subject to the most *o*-fluoro substituents give the greatest frequency shift for a given degree of substitution (e.g., H(2) for monofluorobenzene and H(2) for *m*-difluorobenzene).

From the analysis of the changes in electron population, it is apparent that fluorine withdraws σ electrons, particularly from the ipso carbon atom and from the ortho hydrogens. Fluorine also donates π electrons to the ortho and para carbon atoms. Thus, at the ortho position, the carbon is more negative and the hydrogen is more positive so that the "ionic" contribution to CH bonding is increased. The results are the same with either basis set, but are more pronounced and consistent at the 4-21G level. Therefore, from the population analysis, it is possible to obtain a simple explanation for the decrease in CH bond lengths and the increase in overtone frequency, an explanation which is consistent and additive up to tetrafluoro substitution.

D. Line Widths. The deconvoluted full widths at half maximum, listed in Table II, are comparable to those reported for C_6H_6 , C_6HD_5 , and C_6HF_5 in the gas phase.¹⁹ As we have noted, the line widths from deconvolutions of overlapping peaks are less reliable than those of isolated peaks. Small variations in calculated line widths among peaks within a band can result in a comparable quality of line fit.

One interesting feature of these line widths is the comparison of their change from $\Delta\nu = 3$ to $\Delta\nu = 4$ with that from $\Delta\nu = 4$ to $\Delta\nu = 5$. In all but one of the nine cases corresponding to resolved CH bond types, the bandwidth increase from $\Delta\nu = 4$ to $\Delta\nu = 5$ is considerably less than that from $\Delta\nu = 3$ to $\Delta\nu = 4$. In three of these cases there actually is a decrease. The only exception involves the unresolved peaks corresponding to the meta and para CH bonds in fluorobenzene. The bandwidth increase here would have a significant contribution from the increased energy spacing between the two contributing CH bond types at higher overtones.

A similar trend is observed for the benzene line widths from $\Delta\nu = 3$ to $\Delta\nu = 4$ and from $\Delta\nu = 4$ to $\Delta\nu = 5$.¹⁹ In fact, in benzene, with the exception of an anomaly at $\Delta\nu = 8$, the gas-phase overtone bandwidths decrease from $\Delta\nu = 5$ to $\Delta\nu = 9$.¹⁹ This narrowing has been attributed to a change in the efficiency of intramolecular vibrational energy redistribution, and has been explained by Sibert et al.²⁶ in terms of kinetic energy coupling of the ν quanta local mode overtone state to states with $\nu - 1$ local mode quanta and two quanta in a CCH in-plane wag. The bandwidth narrowing from $\Delta\nu = 5$ to $\Delta\nu = 9$ occurs because the

(22) The correlation of $r_{\text{CH}}^{\text{LM}}$ with $r_{\text{CH}}^{\text{STO-3G}}$, $r_{\text{CH}}^{\text{STO-3G}}$, $r_{\text{CH}}^{4-21\text{G}}$, and $r_{\text{CH}}^{4-21\text{G}}$ is shown here only for the fluorobenzenes. We have larger data sets for all of these correlations in which the improvement in the correlation on going to the split-valence basis set is even greater, and for which the change in bond length extends over a range of 0.020 Å.

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density of these "doorway" states in the energy region of interaction decreases from $\Delta\nu = 5$ to $\Delta\nu = 9$.

Presumably the same mechanism would be operative in the fluorobenzenes. Even given the levels of line-width uncertainty, the present data suggest an earlier onset of bandwidth narrowing than in benzene, perhaps due to a change in the relative frequencies of CH stretching and the CCH in-plane wag. It would be of great interest to extend these preliminary line-width results to higher overtones.

E. $\Delta\nu = 2$ of the Tetrafluorobenzenes. A doublet was observed in the $\Delta\nu = 2$ spectrum of 1,2,4,5-tetrafluorobenzene (Figure 6). The spectra of the other two tetrafluorobenzenes at $\Delta\nu = 2$ are broader and asymmetric. From the observed splitting between the symmetric and antisymmetric fundamentals,²⁷ the expected splitting between the $|2,0\rangle_+$ and $|2,0\rangle_-$ states can be calculated on the basis of the local mode description.²⁸ This calculated splitting is too small to account for the observed spacing between the doublet components of 1,2,4,5-tetrafluorobenzene at $\Delta\nu = 2$. Also, the frequencies of the lower frequency modes make it unlikely that one of the doublet components arises from a combination of the type observed in the dihalomethanes.²⁸

The most likely origin of this splitting, and of the asymmetry in the spectra of the other two tetrafluorobenzenes, is traces of rotational structure.

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V. Conclusions

Peaks due to inequivalent CH bonds are resolved in the overtone spectra of fluorinated benzenes. CH bond lengths from the frequency shifts of the peak positions in these spectra agree with those from geometry-optimized ab initio molecular orbital calculations. In particular, agreement with calculations at the 4-21G level is excellent. These calculations predict the small changes in bond lengths better than calculations at the STO-3G level. Overtone spectra and this type of analysis would appear to provide the best available technique for determining CH bond lengths in molecules of this size.

Substituent-induced charge redistribution can be modelled by an electron population parameter, which describes a CH bond in simple terms of "ionic" and "covalent" parts. Changes in such a parameter correlate very well with changes in CH bond lengths. Moreover, the parameter provides a simple physical explanation of bond-length changes with substitution.

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Registry No. Fluorobenzene, 462-06-6; 1,3-difluorobenzene, 372-18-9; 1,2-difluorobenzene, 367-11-3; 1,4-difluorobenzene, 540-36-3; 1,3,5-trifluorobenzene, 372-38-3; 1,2,3,4-tetrafluorobenzene, 551-62-2; 1,2,4,5-tetrafluorobenzene, 327-54-8; 1,2,3,5-tetrafluorobenzene, 2367-82-0.

Quantum Chemical Interpretation of Oxidation Number as Applied to Carbon and Oxygen Compounds. Numerical Analysis of the Electron Distribution with ab Initio Molecular Orbital Wave Functions

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Abstract: To get quantum chemical interpretation of the oxidation states and oxidation numbers of various atoms, the electron distribution around the carbon, oxygen, and fluorine atoms was analyzed for three series of compounds (i) CH₄, CH₃OH, HCHO, HCOOH, and CO₂, (ii) H₂O and H₂O₂, and (iii) F₂O and F₂O₂ by the ab initio molecular orbital calculations. The difference spherically averaged electron density, $\Delta\rho_0(R) = \rho_0(R) - \sum_i^{\text{atom}} \rho_{0i}(R)$, on a sphere with radius R centered at the atom concerned, was calculated with various qualities of basis sets. The present analysis, together with those previously obtained for sulfur and chlorine compounds, shows that (i) the oxidation states around the carbon atom change stepwise from CH₄ to CO₂ a little less than in the case with the S and Cl compounds, (ii) the oxygen atom can retain the same oxidation state in molecules except in H₂O₂ and fluorine oxides, and (iii) the fluorine atom is the most electronegative but the difference from oxygen is less than generally accepted. These conclusions are almost consistent with the formally assigned classical oxidation numbers.

Introduction

One of the main purposes of the ab initio calculations of molecular electronic states is to elucidate the nature of the chemical bond in terms of quantum chemically defined quantities, so that one can reinterpret traditionally used chemical concepts. With the development of computational techniques and the accumulation of wave functions of high quality, detailed three-dimensional analysis of the electronic distribution over a whole molecule,²⁻⁵

instead of the conventional population analysis,⁶⁻⁸ becomes possible.

The classical concepts of the oxidation state and oxidation number are usually introduced in most textbooks of inorganic chemistry and are even favorably used in the research area of inorganic chemistry.¹⁰ On the other hand, in organic chemistry,

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