

Articles

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Molecular Structures of Gaseous Trifluoromethylsulfurane, CH₃SF₃, and Trifluoro(trifluoromethyl)sulfurane, CF₃SF₃: Experimental Determination by Electron Diffraction and ab Initio Calculations

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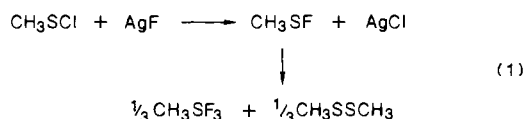
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The structures of gaseous trifluoromethylsulfurane and trifluoro(trifluoromethyl)sulfurane have been determined by electron diffraction. Both molecules have thus been shown to adopt structures based on a trigonal bipyramid centered on the sulfur atom, with the CX₃ group (X = H or F) and lone pair occupying equatorial sites, in conformity with C_{2v} symmetry. The CX₃ group and equatorial S-F bond are found to favor an eclipsed conformation. Salient structural parameters (r_a) are as follows. (i) For CH₃SF₃: r(S-F_{ax}) = 168.9 (0.1), r(S-F_{eq}) = 157.5 (0.5), r(S-C) = 179.0 (1.3), and r(C-H) = 114.2 (1.0) pm; ∠F_{ax}-S-F_{ax} = 174.6 (0.8) and ∠C-S-F_{eq} = 102.9 (0.8)°. (ii) For CF₃SF₃: r(S-F_{ax}) = 167.9 (0.4), r(S-F_{eq}) = 159.6 (1.1), r(S-C) = 191.1 (0.7), and r(C-F)_{mean} = 132.4 (0.2) pm; ∠F_{ax}-S-F_{ax} = 165.2 (2.5), ∠C-S-F_{eq} = 100.7 (1.6), and ∠S-C-F = 107.5 (0.6)°. The experimental results are generally in good agreement with the parameters deduced on the basis of ab initio calculations.

Introduction

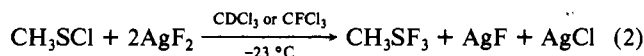
Much effort has been expended on the exploration of the structures and reactivities of substituted fluorophosphoranes of the type X_nPF_{5-n} where X is an organic group,²⁻⁵ chlorine,⁶ or hydrogen.⁷ Such molecules have played an important part as testbeds for the valence-shell electron-pair repulsion (VSEPR) model,⁸ with concepts such as "apicophilicity" evolving from these and related studies.⁹ In contrast, there is a dearth of information about the corresponding sulfuranes X_nSF_{4-n}. Studies have doubtless been inhibited by the comparative difficulty posed by the synthesis of such molecules, by their reactivity (especially with respect to glass), and also by the limited thermal stability, which they display more often than not.

The compound trifluoromethylsulfurane was first identified positively by Gombler and Budenz¹⁰ as a product of the disproportionation of methylsulfenyl fluoride (eq 1). It was reported



to decompose in glass apparatus at 0 °C with the formation of

the corresponding sulfinyl fluoride CH₃S(O)F. Altogether more convenient, however, is the route to the sulfurane pioneered by Forster,¹¹ which involves reaction 2 carried out in an apparatus



fabricated from Teflon-PTFE/FEP. The pure liquid has a half-life on the order of minutes at ambient temperatures; under similar conditions and at a pressure of 5-10 mmHg, the vapor decomposes with a half-life on the order of 15 min. Details of the preparation and physical and chemical properties of the compound will be presented elsewhere.¹¹ A considerable enhancement of thermal stability attends the replacement of CH₃ as a substituent by the perfluoroalkyl group CF₃. Thus, the compound CF₃SF₃ is quite well documented.^{11,12} It too is conveniently synthesized by the action of AgF₂ on the corresponding sulfinyl chloride;¹¹ the neat liquid has a normal boiling point of -7 °C¹² and is stable indefinitely in a fluorocarbon apparatus at ambient temperatures.

Here we describe an investigation of the gaseous fluorosulfurane molecules CH₃SF₃ and CF₃SF₃ whose structures have been determined by electron diffraction. Analysis of the scattering patterns leads us to infer that both molecules emulate not the hypothetical molecule SH₄, which is predicted to have a square-pyramidal geometry, but the related fluorosulfuranes (CF₃)₂SF₂,¹³ FSSF₃,¹⁴ and (CH₃)₂NSF₃¹⁵ by adopting a framework of trigonal-bipyramidal parentage, with the organic group and lone pair occupying equatorial sites and so conforming to the

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Table I. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths

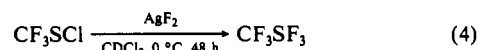
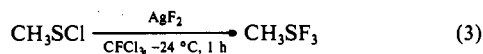
molecule	nozzle-to-plate dist/mm	$\Delta s/$ nm ⁻¹	$s_{\min}/$ nm ⁻¹	$sw_1/$ nm ⁻¹	$sw_2/$ nm ⁻¹	$s_{\max}/$ nm ⁻¹	correln, p/h	scale factor, k^a	electron wavelength/pm ^b
CH ₃ SF ₃	128.35	4	60	80	270	324	0.356	0.731 (11)	5.707
	285.39	2	20	40	122	144	0.484	0.728 (7)	5.706
CF ₃ SF ₃	128.38	4	60	80	244	300	0.303	0.650 (24)	5.722
	285.17	2	20	40	122	144	0.484	0.746 (14)	5.722

^a Figures in parentheses are the estimated standard deviations of the last digits. ^b Determined by reference to the scattering pattern of benzene vapor.

predictions of VSEPR theory.⁸ The experimental findings invite comparison with the results of ab initio calculations.

Experimental Section

Synthesis. Both trifluoromethylsulfurane and trifluoro(trifluoromethyl)sulfurane were synthesized by oxidative fluorination of the corresponding sulfenyl chloride.¹¹ In eq 3, CH₃SCl was prepared by chlo-



ration of CH₃SSCH₃.¹⁶ In eq 4, CF₃SCl was prepared by the fluorination of CCl₃SCl with NaF in tetramethylenesulfone.¹⁷ With the proclivity of the compounds to attack glass, all manipulations were carried out in apparatus fabricated from Teflon-FEP tubing with Teflon-PTFE couplings and needle valves ("Chemcon", supplied by Production Techniques Ltd.); the apparatus was preconditioned by exposure to elemental fluorine at 1 atm of pressure for a period of 8–12 h.

The solution of CH₃SF₃ in CFCl₃ was filtered from the solid AgF₂/AgF/AgCl residue via a PTFE frit and fractionated in vacuo between traps held at -33, -65, and -196 °C. The sulfurane collected in the -65 °C trap. The trifluoromethyl derivative was manipulated in a similar manner, except that fractional condensation entailed trap temperatures of -95, -160, and -196 °C, with the sulfurane collecting in the -160 °C trap. The purities of the compounds were assessed by reference to the ¹⁹F NMR spectra^{10,11,12c} of CFCl₃ solutions (as well as the ¹H NMR spectrum in the case of CH₃SF₃^{10,11}), and to the IR spectra of the vapors.^{11,12} The samples of CH₃SF₃ were thus shown to be free from detectable impurity, whereas those of CF₃SF₃ were shown to be contaminated by small amounts of CF₃SSCF₃ and CF₃SF₃ (<5%) from which they could not be freed entirely, even by repeated fractionation. The compounds were stored at 77 K in preconditioned Teflon-FEP ampules, each closed by a PTFE needle valve.

Electron-Diffraction Measurements. Electron-scattering patterns were recorded on Kodak Electron Image plates by using the Edinburgh gas diffraction apparatus.¹⁸ Nozzle-to-plate distances were ca. 128 and 285 mm and the accelerating voltage was ca. 44 kV (electron wavelength ca. 5.7 pm). The sample of CH₃SF₃ was held at 0 °C, and the sample of CF₃SF₃ at -78 °C; from the Teflon-FEP ampule containing each of the samples the vapor gained access to the nozzle of the diffraction apparatus (at room temperature) via a Teflon-stainless-steel pressure coupling and a stainless-steel needle valve. To cater to the high reactivity of the molecules, and the thermal fragility of CH₃SF₃ in particular, the inlet system was conditioned with the compounds prior to any measurements of the electron-diffraction patterns. In addition, control experiments were carried out in a stainless-steel apparatus to simulate passage of the vapor through the inlet system of the electron-diffraction assembly, and the survival of the samples was checked by monitoring their ¹H^{10,11} and/or ¹⁹F^{10,11,12c} NMR spectra. The precise nozzle-to-plate distances and electron wavelengths were determined from scattering patterns for benzene vapor recorded immediately before or after the sample patterns. Details are given in Table I, together with the weighting functions used to set up the off-diagonal weight matrices, the correlation parameters, and final scale factors.

Details of the electron-scattering patterns were collected in digital form by using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described elsewhere.¹⁹ Calculations made use of the programs for data reduction¹⁹ and least-squares refine-

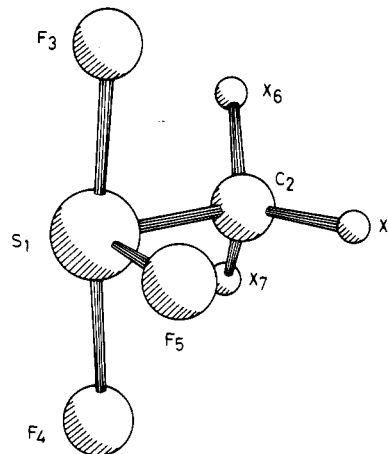


Figure 1. Perspective view of the molecule CH₃SF₃ (X = H) in the optimum refinement of the electron-diffraction data, showing also the numbering of the atoms in the structural model used for both the CX₃SF₃ molecules (X = H or F).

ment²⁰ described previously, the complex scattering factors being those listed by Schäfer et al.²¹

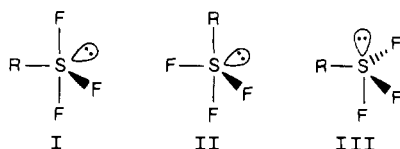
Ab Initio Calculations. All calculations were made by using the ab initio gradient technique²² and the computer program TEXAS.²³ Optimized geometries were obtained for the molecules SH₄, CH₃SH₃, CH₃SF₃, and CF₃SF₃ (two conformers). Except as noted, full optimization of the calculations (4-21-S*) exploited standard procedures.^{24,25} A 3-3-21 basis set,²⁶ which is double- ζ in the valence shell, augmented with a set of d functions with orbital exponent 0.8, was used for the sulfur atom. The standard 4-21 basis²⁵ was used for carbon and fluorine, and a 21 set for hydrogen. On occasion, where noted subsequently, a second set of d functions with orbital exponent 0.2 was added to the sulfur atom, or a set of p functions with exponent 0.75 was added to hydrogen. Optimization of geometries was continued until all residual forces were less than 0.004 mdy, corresponding to expected geometry changes considerably less than 1 in the last digit quoted. In the case of CF₃SF₃, calculations which allowed for electron correlation (MP2/6-31G*//MP2/6-31G*) were also performed by using the program GAUSSIAN 82.²⁷ The 6-31G* basis set includes d functions on all atoms.

Results

(a) Experimental Results: Structure Refinement. The ¹H and ¹⁹F NMR spectra of the sulfuranes CH₃SF₃ and CF₃SF₃¹⁰⁻¹² imply similar structures for the two molecules, each with two inequivalent fluorine sites. The spectral patterns can be reconciled with any one of the three structures I–III, although the ¹⁹F chemical shifts

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elicit strong circumstantial evidence for I. We have measured the ^{19}F NMR spectrum of CF_3SF_3 vapor (at a pressure close to 1 atm) and found it to be similar in all essential respects to that of a CFCl_3 solution,^{10,11,12c} with no signs to betray fluxionality or the presence of more than one conformer. The relatively low symmetry of such a molecule, allied to problems of vibrational mixing, obviates any unequivocal structural conclusion based on its vibrational spectra, but the IR spectra displayed by both the gaseous fluorosulfuranes^{11,12} have much in common with those of the fluorophosphoranes $(\text{CH}_3)_2\text{PF}_3$ ²⁸ and Cl_2PF_3 ⁶ and are therefore also consistent with structure I.

Inspection of the radial-distribution curves derived from the electron-scattering patterns of the gaseous sulfuranes reveals features incompatible with either of the structures II or III. Accordingly, we have adopted as a basis for calculating the electron-scattering intensities a model along the lines of I, with a trigonal-bipyramidal framework accommodating the organic group CX_3 ($\text{X} = \text{H}$ or F) and the lone pair in the equatorial plane. In all, the model required 12 independent geometrical parameters. With reference to Figure 1, these comprised (i) a mean S-F distance, $r(\text{S-F})_{\text{mean}}$, (ii) the difference $\Delta(\text{S-F}) = r(\text{S-F}_{\text{ax}}) - r(\text{S-F}_{\text{eq}})$ between the axial (ax) and equatorial (eq) S-F bonds, (iii) the S-C distance, $r(\text{S-C})$, (iv) a mean C-X distance, $r(\text{C-X})_{\text{mean}}$, and (v) the difference $\Delta(\text{C-X}) = r(\text{C-X}_{6,7}) - r(\text{C-X}_8)$ between the out-of-plane and in-plane C-X distances. In addition, there were seven angular parameters, viz. (vi) $\angle\text{F}_{\text{ax}}\text{-S-F}_{\text{ax}}$, (vii) $\angle\text{C-S-F}_{\text{eq}}$, (viii) $\angle\text{C-S-F}_{\text{ax}}$, (ix) $\angle\text{S-C-X}_{\text{mean}}$, (x) the difference $\Delta\theta = \angle\text{S-C-X}_{6,7} - \angle\text{S-C-X}_8$, (xi) $\angle\text{X}_6\text{-C-X}_7$, and (xii) a twist angle τ defined by the dihedral angle of the unit $\text{F}_5\text{-S-C-X}_8$. Such a model accounts satisfactorily for the experimental radial-distribution curves (see Figure 2).

(i) CH_3SF_3 . The radial-distribution curve derived from the scattering pattern of CH_3SF_3 shows prominent, well-defined peaks near 115, 165, and 340 pm. The first two correspond to scattering from C-H- and S-F/S-C-bonded atom pairs, respectively, whereas the third corresponds to scattering from the $\text{F}_{\text{ax}}\cdots\text{F}_{\text{ax}}$ nonbonded pair. A broad feature centered at ca. 240 pm, with a shoulder at ca. 270 pm, is identifiable with scattering from $\text{F}_{\text{ax}}\cdots\text{F}_{\text{eq}}$, $\text{F}_{\text{ax}}\cdots\text{C}$, and $\text{F}_{\text{eq}}\cdots\text{C}$ nonbonded pairs.

(ii) CF_3SF_3 . The radial-distribution curve for CF_3SF_3 is characterized by peaks at about 135, 170, 230/260, and 340/370 pm. The first two are attributable to scattering from C-F-bonded and S-F-bonded atom pairs, respectively. The broader, composite feature at 230/260 pm takes account of the scattering due to $\text{F}_{\text{ax}}\cdots\text{F}_{\text{eq}}$, $\text{F}_{\text{ax}}\cdots\text{C}$, $\text{F}_{\text{eq}}\cdots\text{C}$, and $\text{S}\cdots\text{F}_c$ nonbonded pairs ($\text{F}_c = \text{F}$ of CF_3 group); that at 340/370 pm takes account of the scattering due to $\text{F}_{\text{ax}}\cdots\text{F}_{\text{ax}}$, $\text{F}_{\text{ax}}\cdots\text{F}_c$, and $\text{F}_{\text{eq}}\cdots\text{F}_c$ nonbonded pairs. The peak associated with the S-C-bonded distance is partially hidden, appearing as a shoulder at ca. 190 pm.

Molecular scattering intensities have been calculated by established procedures, and the molecular structures have been refined on the basis of the model described by a full-matrix least-squares analysis. For neither molecule are the vibrational properties sufficiently well defined to admit the possibility of "shrinkage" corrections, but there is no reason to suppose that such corrections would alter significantly the results of the analysis.

The majority of the independent geometrical parameters used to define the structures of CH_3SF_3 and CF_3SF_3 have yielded to simultaneous refinement. The exceptions were $\Delta(\text{C-X})$, $\Delta\theta$, and $\angle\text{X}_6\text{-C-X}_7$, the magnitudes of which had to be fixed for both molecules, and $\angle\text{S-C-H}$, which likewise had to be fixed for the methyl derivative. Simultaneous refinement also eluded the dihedral angle τ , defining the twisting of the CH_3 group with respect

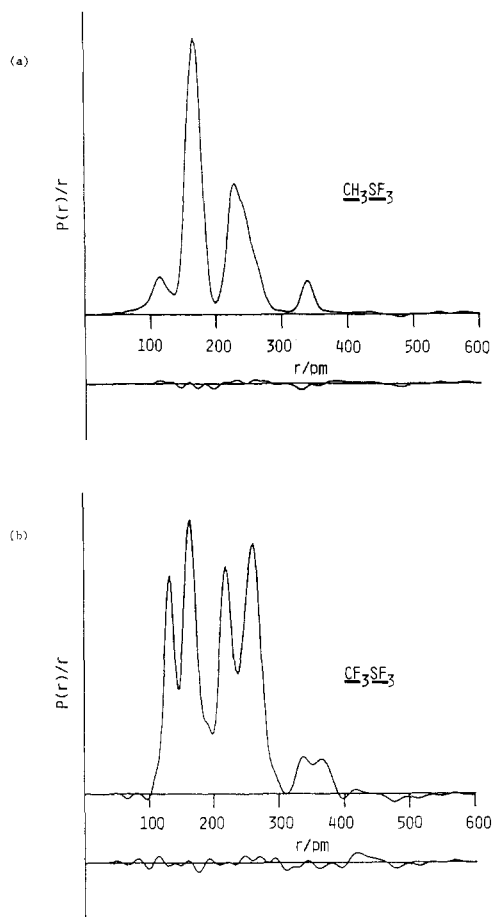


Figure 2. Observed and difference radial-distribution curves, $P(r)/r$ vs r , (a) for CH_3SF_3 ; (b) for CF_3SF_3 . Before Fourier transformation the data were multiplied by $s \exp\{(-0.00002s^2)/(Z_{\text{S}} - f_{\text{S}})(Z_{\text{F}} - f_{\text{F}})\}$.

to the SF_3 fragment, but this parameter was varied in a stepwise manner; the optimum R factor was thus found with $\tau = 0^\circ$. Hence, the preferred conformation of CH_3SF_3 is that in which the S-F₅ eclipses the C-H₈ bond, and the refinement calculations indicate a similar situation for CF_3SF_3 . Independent refinement was also possible for seven amplitudes of vibration in CH_3SF_3 and nine such amplitudes in CF_3SF_3 . Otherwise, we have drawn on the precedents set by related molecules, e.g. CH_3PF_4 ,⁴ CF_3PF_4 ,²⁹ SF_4 ,³⁰ and $(\text{CF}_3)_2\text{SF}_2$,¹³ to assign reasonable values to the remaining amplitudes.

The success of the refinements may be gauged by the difference between the experimental and calculated radial-distribution curves (see Figure 2). Figure 3 offers a similar comparison between the experimental and calculated molecular scattering. The structural details and vibrational amplitudes of the optimum refinements, corresponding to $R_G = 0.07$ ($R_D = 0.05$) for CH_3SF_3 and $R_G = 0.13$ ($R_D = 0.09$) for CF_3SF_3 , are listed in Table II. The estimated standard deviations allow for the effects of correlation and take account also of systematic errors in the electron wavelength, nozzle-to-plate distances, etc. Despite appreciable correlation of certain parameters, e.g. those defining the S-F and S-C distances (see Table III), the main features of both structures are well defined. That the level of agreement for CF_3SF_3 should be somewhat inferior to that for CH_3SF_3 seems mainly to reflect "noisier" data more than any specific discrepancy; calculations taking account of the potential impurities CF_3SSCF_3 and CF_3SF_5 ruled out any significant contribution to the scattering from either of these sources. We also carried out refinements allowing for the coexistence of isomers of CF_3SF_3 with structures I and II (i.e. with equatorial and axial CF_3 groups, respectively). As is in-

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Table II. Molecular Parameters Deduced from the Electron-Diffraction Patterns of CH₃SF₃ and CF₃SF₃

(a) Geometrical Parameters (Distances in pm, Angles in deg, r_a Structures) ^a				
param		CH ₃ SF ₃	CF ₃ SF ₃	
p_1	$r(\text{S-F})_{\text{mean}}$	165.1 (2)	165.1 (2)	
p_2	$\Delta r(\text{S-F}) (r_{\text{ax}} - r_{\text{eq}})$	11.4 (6)	8.3 (14)	
p_3	$r(\text{S-C})$	179.0 (13)	191.1 (7)	
p_4	$r(\text{C-X})_{\text{mean}}^b$	114.2 (10)	132.3 (2)	
p_5	$\Delta r(\text{C-X})^{b,c}$	0.0 ^d	-0.6 ^d	
p_6	$\angle \text{F}_{\text{ax}}-\text{S}-\text{F}_{\text{ax}}$	174.6 (8)	165.2 (25)	
p_7	$\angle \text{F}_{\text{eq}}-\text{S}-\text{C}$	102.9 (8)	100.7 (16)	
p_8	$\angle \text{F}_{\text{ax}}-\text{S}-\text{C}$	89.2 (9)	86.7 (6)	
p_9	$\angle \text{F}_{\text{ax}}-\text{S}-\text{F}_{\text{eq}}^e$	87.6 (4)	84.1 (13)	
p_{10}	$\angle \text{S-C-X}_{\text{mean}}^b$	108.0 ^d	107.5 (6)	
p_{11}	$\Delta\theta = \angle \text{S-C-X}_{6,7} - \angle \text{S-C-X}_{8}^{b,c}$	0.0 ^d	2.0 ^d	
p_{12}	$\angle \text{X-C-X}^{b,c}$	112.0 ^d	108.5 ^d	
p_{13}	τ , twist angle ^c	0.0 ^{d,f}	0.0 (5)	

(b) Interatomic Distances (r_a /pm) and Amplitudes of Vibration (u /pm) ^{a,g}					
param	CH ₃ SF ₃		CF ₃ SF ₃		
	dist	amplitude	dist	amplitude	
$r(\text{S-F}_{\text{ax}})$	168.9 (1)	4.6 (13)	167.9 (4)	6.9 (7)	
$r(\text{S-F}_{\text{eq}})$	157.5 (5)		159.6 (11)		4.5 ^d
$r(\text{S-C})$	179.0 (13)	6.5 ^d	191.1 (7)	3.7 (6)	
$r(\text{C-X}_{6,7})^{b,c}$	114.2 (10)		132.1 (2)		
$r(\text{C-X}_8)^{b,c}$	114.2 (10)	10.0 ^d	132.7 (2)	7.9 (6)	
$r(\text{S}\cdots\text{X}_{6,7})^{b,c}$	240.3 (13)		264.0 (5)		
$r(\text{S}\cdots\text{X}_8)^{b,c}$	240.3 (13)	6.7 (5)	261.2 (5)	5.5 (15)	
$r(\text{F}_{\text{ax}}\cdots\text{F}_{\text{ax}})$	337.5 (2)		332.9 (10)		
$r(\text{F}_{\text{ax}}\cdots\text{F}_{\text{eq}})$	226.2 (2)	5.6 (3)	219.4 (12)	8.4 (5) ^h	
$r(\text{F}_{\text{ax}}\cdots\text{C})$	244.4 (5)		246.9 (9)		
$r(\text{F}_{\text{eq}}\cdots\text{C})$	263.6 (6)	4.6 (7)	270.7 (19)	8.0 ^d	

^a Figures in parentheses are the estimated standard deviations of the last digits. ^b X = H or F. ^c For definition see text and Figure 1. ^d Fixed. ^e Dependent parameter. ^f Refined earlier: see text. ^g Other distances between the atoms of the CX₃ and those of the SF₃ group were also included in the refinements, but are not listed here. ^h Tied also to $u(\text{X}\cdots\text{X})$.

Table III. Portions of the Least-Squares Correlation Matrices Listing Off-Diagonal Elements with Absolute Values $\geq 50\%$

(a) For CH ₃ SF ₃					
p_2	p_3	p_7	p_8	$u(\text{S-F/C})$	
-86	-76		67	82	p_1
	89	-59	-83	-93	p_2
				-95	p_3
	-61	76	78		p_6
	-76			70	p_7
	-94	83		-89	p_8

(b) For CF ₃ SF ₃						
p_1	p_2	p_3	p_6	p_8	$u(\text{C-X})$	$u(\text{S}\cdots\text{X})$
-64						p_2
-57				86		p_6
		-51				p_7
		-61	68	52		p_{10}
60	-86					$u(\text{S-F})$
				65	51	k_2^a

^a Scale factor.

variably the case with problems of this sort, it is impossible to state definitely that the form with the axial CF₃ group (II) is completely absent. However, inclusion of small amounts of this isomer did not make any significant difference to the fit to the experimental data, and inclusion of more than 20% led to a rapid deterioration of the fit.

(b) Ab Initio Calculations: Calculated Structures. The optimized geometry deduced from ab initio calculations on the parent sulfurane SH₄ is characterized not by C_{2v} but by C_{4v} symmetry, with all S-H distances equal at 137.3 pm and angles of 87.8° between adjacent S-H bonds (i.e. 157.5° between opposing bonds).

The geometry thus conforms to a shallow square-based pyramid. It is to be noted that this result was obtained with quite a modest-sized basis set—smaller than the one used by Schaefer et al.³¹—but, as pointed out by Veillard and several others,³² the use of polarization functions on sulfur is a necessity. The experience gained from a study of amine group nonplanarity³³ led us to try adding a set of p functions to the hydrogen atoms, but the symmetry of the optimum geometry remained unchanged and the effect on the HSH angles was insignificant.

The optimized structure of the molecule CH₃SH₃ resembles that of SH₄ quite closely in its angular geometry (see Table IV), with the opposing pairs of bonds S-H/S-H and S-H/S-C subtending angles of 153.3 and 150.5°, respectively. On the other hand, the two opposing S-H bonds are longer by 1 pm and the unique S-H bond "trans" to the CH₃ substituent is shorter by 0.5 pm than the four equivalent bonds in SH₄. Because the geometry appeared to anticipate some of the structural features of the fluorosulfuranes, a single run was made with a second set of d functions on the sulfur atom, a single set of d functions on carbon, and a set of p functions on hydrogen. The forces that would affect the angles were altered but slightly, and the predicted changes did not affect the molecular symmetry (C_s) while changing individual angles by no more than a few degrees. The angles predicted by the simpler basis should therefore be essentially correct.

The structures computed for the CSF₃ frameworks of the two fluorosulfuranes CH₃SF₃ and CF₃SF₃ resembled each other quite closely and are generally in pleasingly good agreement with the structures determined by electron diffraction (see Table IV). Thus, the main features of the experimentally determined structures are reproduced by the calculations, even down to the eclipsing of the CX₃ group (X = H or F) by the equatorial S-F bond. The one parameter that proved difficult to reproduce was the C-S bond length in CF₃SF₃. The simpler calculations—at the 4-21-S* level—gave results significantly out of line for this distance (184.0 pm, as compared with the experimental value of 191.1 pm). Calculations at a higher level of sophistication, with due allowance for electron correlation (MP2/6-31G**//MP2/6-31G*), yielded an increased C-S distance of 187.1 pm, in closer agreement with, but still some 4 pm short of, the experimental result. This is not the first time that such ab initio calculations have run into difficulty in their anticipation of the effects of fluorination at carbon bound to a second-row atom.^{34,35} For example, the Si-C bond is attenuated by 5.9 pm when the CH₃ substituent in CH₃SiH₃ is replaced by CF₃, whereas ab initio calculations predict attenuation by only 1.5 pm; the corresponding change from CH₃SiF₃ to CF₃SiF₃ is likewise underestimated by the calculations (8.5 vs 3.8 pm).³⁴ Further elaborate computations were considered to be unduly extravagant use of computer time, and the calculations were therefore terminated at this level.

In view of the conformational preferences that the phosphoranes (CF₃)_nPF_{5-n} ($n = 1$ or 2) are reported to show,²⁹ with the CF₃ groups having the capacity to oust fluorine from the axial sites, we carried out a trial calculation on a second isomer of CF₃SF₃ having structure II, with axial CF₃ and F substituents and the other two F atoms sharing the equatorial plane with the lone pair. For a structure such as III, with an axially sited lone pair, there is no experimental precedent, and all the theoretical signs point to a significantly higher energy. The calculations on CF₃SF₃, structure II, employed a 6-31G* basis without electron correlation. They showed that there is indeed a minimum in the potential energy surface corresponding to structure II, albeit giving an optimized equilibrium form 64.0 kJ mol⁻¹ less stable than structure

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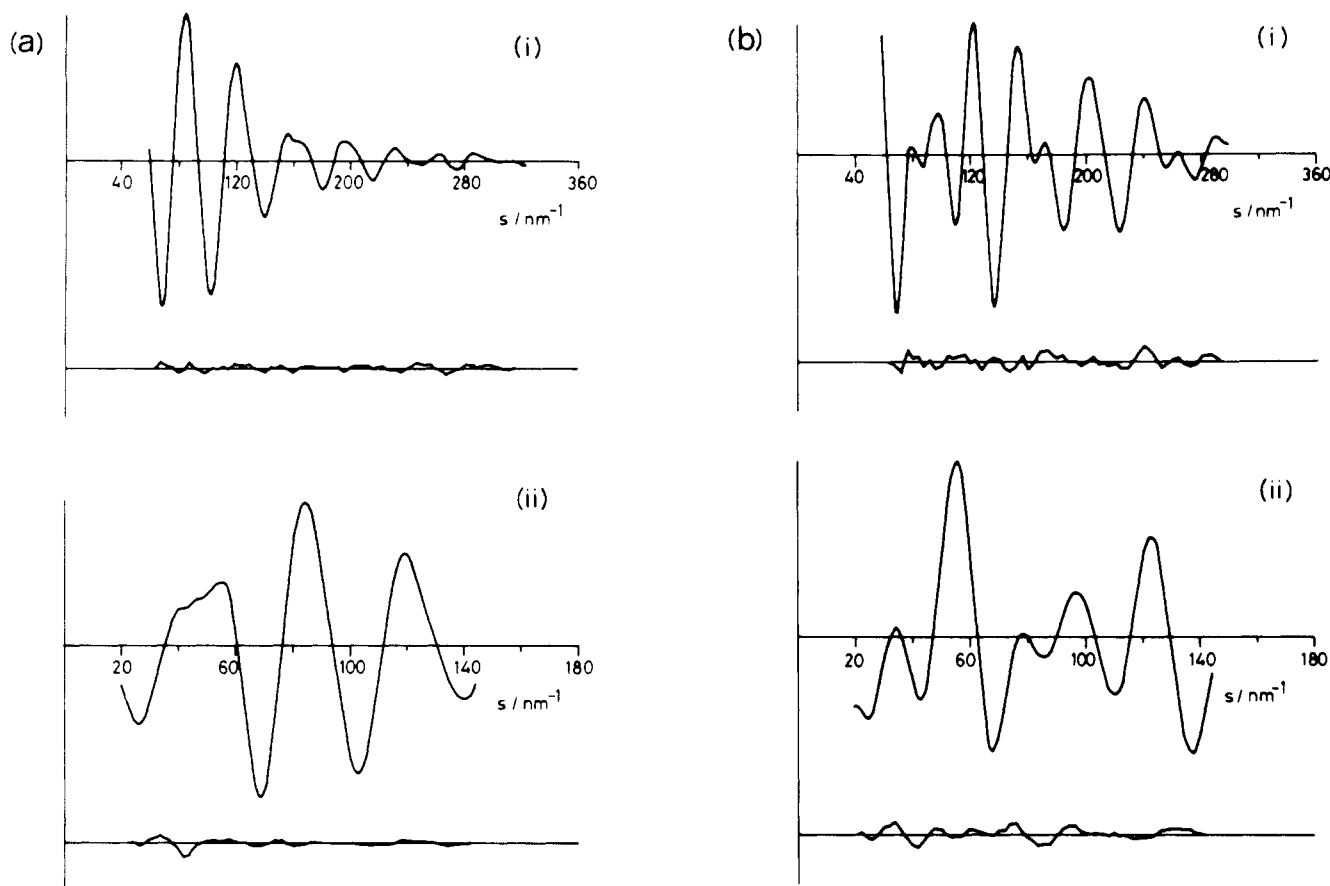


Figure 3. Experimental and final difference molecular-scattering intensity curves (a) for CH_3SF_3 ; (b) for CF_3SF_3 . Nozzle-to-plate distance: (i) 128.35 (CH_3SF_3) or 128.38 mm (CF_3SF_3); (ii) 285.39 (CH_3SF_3) or 285.17 mm (CF_3SF_3).

Table IV. Calculated Geometric Parameters (Distances in pm; Angles in deg) for the Sulfuranes CH_3SH_3 , CH_3SF_3 , and CF_3SF_3 and Comparison with the Corresponding Experimental Parameters for the Fluorosulfuranes

param ^a	CH_3SH_3 basis 4-21-S*	CH_3SF_3		CF_3SF_3		
		basis 4-21-S*	exptl	basis 4-21-S*	basis MP2/6-31G**// MP2/6-31G*	exptl
$r(\text{S}-\text{Y}_{\text{ax}})$	139.0	167.4	168.9 (1)	164.6	168.4	167.9 (4)
$r(\text{S}-\text{Y}_{\text{eq}})$	137.4	157.9	157.5 (5)	156.7	160.0	159.6 (11)
$r(\text{S}-\text{C})$	187.0	177.5	179.0 (13)	184.0	187.1	191.1 (7)
$r(\text{C}-\text{X}_{6,7})^b$	108.7	107.3	114.2 (10)	133.9	132.8	132.1 (2)
$r(\text{C}-\text{X}_8)^b$	108.5	108.2	114.2 (10)	134.5	133.1	132.7 (2)
$\angle \text{Y}_{\text{ax}}-\text{S}-\text{Y}_{\text{ax}}$	153.3	168.5	174.6 (8)	166.5	169.7	165.2 (25)
$\angle \text{Y}_{\text{eq}}-\text{S}-\text{C}$	150.5	105.1	102.9 (8)	104.1	101.5	100.7 (16)
$\angle \text{Y}_{\text{ax}}-\text{S}-\text{C}$	87.1	88.0	89.2 (9)	86.0	87.3	86.7 (6)
$\angle \text{Y}_{\text{ax}}-\text{S}-\text{Y}_{\text{eq}}$	86.2	85.4	87.6 (4)	85.7	86.3	84.1 (13)
$\angle \text{S}-\text{C}-\text{X}_{6,7}^b$	107.5	108.9	108.0 ^c	110.1	110.0	108.2 (6)
$\angle \text{S}-\text{C}-\text{X}_8^b$	110.9	107.0	108.0 ^c	108.2	108.3	106.2 (6)
$\angle \text{X}_6-\text{C}-\text{X}_7^b$	111.2	112.6	112.0 ^c	108.5	108.5	108.5 ^c
τ , twist angle ^b	0.2	0.2	0.0 ^c	0.3	0.0	0.0 (5)

^aX = H or F; Y = H or F. ^bFor definition see text and Figure 1. ^cFixed.

I. Hence, there seems to be a significant energetic preference for equatorial siting of the organic group in molecules of the type RSF_3 , and it would be interesting to carry out similar calculations on phosphoranes like $(\text{CF}_3)_2\text{PF}_3$ to see how and why these differ from the corresponding sulfuranes.

Discussion

The electron-diffraction patterns of the fluorosulfurane molecules CH_3SF_3 and CF_3SF_3 imply that the organic group and lone pair occupy equatorial sites of a framework approximating not to a square pyramid, as in SH_4 , but to a trigonal bipyramid centered on the sulfur atom. The CSF_3 skeleton of each molecule thus conforms to C_s symmetry. This finding may come as no surprise. Not only is it in accord with the inferences drawn from the NMR and vibrational spectra,¹⁰⁻¹² it complies with VSEPR predictions.⁸ It is in keeping too with the suggested order of

"apicophilicity",⁹ $\text{F} > \text{Cl}, \text{Br} > \text{CF}_3 > \text{OR}, \text{SR}, \text{NR}_2, \text{R}$, although doubts about the universality of this order have been cast by the structures of the gaseous molecules $(\text{CF}_3)_n\text{PX}_{5-n}$ ($\text{X} = \text{F}, n = 1$ or 2 ; $\text{X} = \text{Cl}, n = 2$ or 3)²⁹ determined by electron diffraction.

The structures of CH_3SF_3 and CF_3SF_3 resemble most obviously those of $(\text{CH}_3)_2\text{NSF}_3$ ¹³ and the mixed-valence sulfurane FSSF_3 ,¹⁴ while also inviting comparisons with those of SF_4 ,³⁰ $(\text{CF}_3)_2\text{SF}_2$,¹³ the sulfur(VI) compound $\text{CF}_3\text{C}\equiv\text{SF}_3$,³⁶ the phosphoranes $(\text{CX}_3)_n\text{PF}_{5-n}$ ($\text{X} = \text{H}$ or $\text{F}; n = 1$ or 2),^{4,29} and a variety of other compounds containing CH_3-S and CF_3-S moieties. Collation of the dimensions of these molecules (see Tables V and VI) is revealing for the light it sheds, first, on the stereochemical properties of sulfuranes and, second, on the effects of changing the character

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Table V. Skeletal Dimensions of Molecules of the Types X_nSF_{4-n} and X_nPF_{5-n}, Where n = 0–2, and X = CH₃, CF₃, or SF, As Determined by Electron Diffraction (Distances in pm, Angles in deg; r_a Structures, Except As Noted)

molecule	r(E–C) ^a	r(E–F _{ax}) ^a	r(E–F _{eq}) ^a	∠F _{ax} –E–F _{ax} ^a	∠X _{eq} –E–F _{eq} ^a	ref
SF ₄		164.3 (5)	154.2 (5)	176.8 (25)	103.8 (6)	30
CH ₃ SF ₃	179.0 (13)	168.9 (1)	157.5 (5)	174.6 (8)	102.9 (8)	this work
CF ₃ SF ₃	191.1 (7)	167.9 (4)	159.6 (11)	165.2 (25)	100.7 (16)	this work
FSSF ₃ ^b		167.3 (7) ^c	156.9 (8)	167.0 ^d	104.9 (14)	14
(CH ₃) ₂ NSF ₃		167.0 (7)	156.3 (9)	174.0 (12) ^d	104.6 (10)	15
(CF ₃) ₂ SF ₂	188.8 (4)	168.1 (3)		173.9 (8)		13
PF ₅		158.0 (2)	153.2 (3)	180	120	3
CH ₃ PF ₄	178.0 (5)	161.2 (4)	154.3 (4)	176.4 (8)	115.6 (18) ^e	4
CF ₃ PF ₄ ^f	188.1 (8)	157.3 (7)	153.7 (5)	180 ^e	117.4 (34) ^e	29

^aE = S or P; X = F, CH₃, CF₃, or SF. ^br_a⁰ values based on combined electron-diffraction and microwave studies. ^cMean value: see text. ^dDependent parameter. ^eX = F. ^fEquatorial conformer. ^gValue not refined.

Table VI. Dimensions of Molecules Containing CH₃ and CF₃ Groups Bound to Sulfur(II) and Sulfur(IV) Centers (Distances in pm; r_a Structures, Except As Noted)

valence state of sulfur	molecule	r(S–C)	r(C–X) _{mean} ^a	ref
4	CH ₃ SF ₃	179.0 (13)	114.2 (10)	this work
4	(CH ₃) ₂ SO	180.8 (4) ^b	107.4 (17) ^b	39
2	CH ₃ SH	181.9 (5) ^c	109.2 (10) ^c	37a
2	(CH ₃) ₂ S	180.2 (2) ^d	109.2 (5) ^d	37b
2	CH ₃ SSCH ₃	180.6 (2)	109.0 (7)	37c
4	CF ₃ SF ₃	191.1 (7)	132.4 (2)	this work
4	(CF ₃) ₂ SF ₂	188.8 (4)	131.7 (2)	13
2	CF ₃ SH	180.0 (5)	133.5 (3)	38a
2	CF ₃ SF	180.5 (3) ^e	133.1 (2) ^e	38b
2	CF ₃ SCl	182.4 (6) ^e	133.0 (2) ^e	38b
2	CF ₃ SBr	181.4 (6) ^e	133.1 (3) ^e	38c
2	(CF ₃) ₂ S	181.9 (3) ^e	133.0 (2) ^e	38b

^aX = H or F. ^br_a structure deduced from combined microwave and force-field analysis. ^cr_o structure deduced from microwave studies. ^dr_s structure deduced from microwave studies. ^er_a⁰ structure deduced from combined electron-diffraction and vibrational studies.

of the organic substituent. Four features catch the eye.

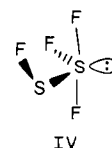
(i) Replacement of fluorine by a less electronegative substituent at one of the equatorial sites of SF₄ results in a lengthening of all the surviving S–F bonds—axial and equatorial alike—with respect to the parent molecule, SF₄.³⁰ The sulfuranes thus differ from the related phosphoranes in two ways. In the first place, the replacement of fluorine in PF₅ by CH₃ results in significant attenuation of *only* the axial P–F bonds; second, the replacement of fluorine in PF₅ by CF₃ evokes little change in the lengths of any of the remaining P–F bonds. The greater, but less selective, sensitivity of the S–F bonds of sulfuranes to the displacement of fluorine by a less electronegative substituent finds no obvious explanation in terms of either VSEPR⁸ or steric arguments. The cause probably lies with the nature of the bonding orbitals that enjoy a more-or-less “hybrid” character under the relatively low symmetries which characterize the fluorosulfurane molecules.

(ii) Replacement of hydrogen by fluorine at the carbon atom is accompanied by a lengthening of the C–S bond by 12.1 pm. In this respect the sulfuranes CH₃SF₃ and CF₃SF₃ follow the same pattern as the phosphoranes CH₃PF₄ [r(C–P) = 178.0 pm]⁴ and CF₃PF₄ [r(C–P) = 188.1 pm].²⁹ The attenuation, already alluded to as an Achilles’ heel of the ab initio calculations, can be rationalized qualitatively in terms of polar contributions to the bonding. In CH₃SF₃, this polar contribution is attractive (C^{δ-}–S^{δ+}): in CF₃SF₃, it is repulsive (C^{δ+}–S^{δ+}). It may be remarked that the effect seems to be a general one in fluoride derivatives CX₃EF_n of the heavier typical elements E and that exchanging CH₃ (X = H) for CF₃ (X = F) results in elongation of the C–E bond, typically by 6–10 pm.³⁴

(iii) The switch from the sulfur(II) compounds CH₃SH^{37a} and (CH₃)₂S^{37b} to the sulfur(IV) compound CH₃SF₃ is marked by

little change in the C–S bond length (ca. 180 pm): the switch from CF₃SH,^{38a} CF₃SF,^{38b} CF₃SCl,^{38b} CF₃SBr,^{38c} or (CF₃)₂S^{38b} to CF₃SF₃ is marked by an increase in the C–S bond length amounting to about 10 pm. Hence, it *appears* that the increased positive charge associated with the sulfur(IV) center makes itself felt significantly only through the repulsive polar contributions (q.v.) and not perceptibly (at least, within the limits of experimental error) through any change in the attractive polar contributions. Once again, however, the “hybrid” character of the bonding orbitals in a molecule like CF₃SF₃ with C_v symmetry and the competition between two electronegative substituents (F and CF₃) is bound to obscure the true source(s) of this effect.

(iv) The bond angles of the CSF₃ skeletons of the fluorosulfuranes show the expected departures from the values appropriate to a regular trigonal bipyramid. Thus, the axial S–F bonds are bent toward the equatorial substituents to give F_{ax}–S–F_{ax} bond angles of 174.6 (CH₃SF₃) and 165.2° (CF₃SF₃), whereas the equatorial S–F and S–C bonds are bent toward each other to give F_{eq}–S–C_{eq} bond angles of 102.9 (CH₃SF₃) and 100.7° (CF₃SF₃). In angular terms, CH₃SF₃ resembles closely the parent molecule SF₄,³⁰ except that the displacement of the axial S–F bonds is lopsided, being confined to a plane almost coincident with the equatorial S–F bond (while maintaining a C–S–F_{ax} bond angle close to 90°). In contrast, CF₃SF₃ exhibits substantially larger departures from the ideal bond angles of 180 and 90° (a feature quite at odds with what we would have been led to expect by the VSEPR model⁸), and the plane defined by its axial S–F bonds falls *between* the equatorial bonds (albeit closer to the S–F than the S–C bond). The equatorial moiety shows a regular decrease in the bond angle at sulfur in the series SF₄³⁰ > CF₃SF₃ > (CF₃)₂SF₂¹³ (see Table V). More surprising is the relatively irregular trend exhibited in the same series by the axial F–S–F moiety, with the bond angle at sulfur varying in the order SF₄³⁰ > CF₃SF₃ < (CF₃)₂SF₂.¹³ However, the anomalous position of CF₃SF₃ in this sequence is not without precedent. For FSSF₃, which incorporates an equatorial SF group, also displays an unusually compressed F_{ax}–S–F_{ax} bond angle (about 167°), although, unlike either CH₃SF₃ or CF₃SF₃, it also sports inequivalent axial S–F bonds differing in length by almost 10 pm.¹⁴ Here we have reached the limit in the process of descending symmetry having its origin in a regular (D_{3h}) trigonal bipyramid. The difference between the axial S–F bonds in FSSF₃ testifies to the loss of the last genuine symmetry element, i.e. the plane containing the equatorial substituents (see IV), so that there is no longer any



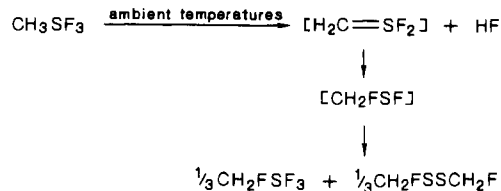
distinction in symmetry between axial and equatorial bonds. That

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distinction has already been partially eliminated in a C_{2v} molecule like SF_4 or $(CF_3)_2SF_2$ (with $2a_1 + b_1 + b_2$ σ -type 1-electron bonding MO's, where the a_1 orbitals span both axial and equatorial ligands), and relaxed still further in a C_s molecule like CF_3SF_3 (with $3a' + a''$ σ -type bonding MO's, where the a' orbitals span both axial and equatorial ligands).

We are unsure of the significance to be attached to the C-H bond length in CH_3SF_3 , which, according to our analysis of the electron-diffraction pattern, is 4-5 pm longer than the corresponding distance in other methyl-sulfur compounds, e.g. CH_3SH ,^{37a} CH_3SSCH_3 ,^{37c} and $(CH_3)_2SO$.³⁹ Such an attenuation is anticipated neither by our ab initio calculations nor by the vibrational properties displayed by the CH_3SF_3 molecule¹¹ that parallel quite closely those of CH_3SH ,⁴⁰ at least with respect to the vibrations localized mainly within the CH_3 group. Moreover, there is no echo of anything similar in the dimensions of the CF_3 group as it occurs in the molecules CF_3SF_3 and CF_3SX ($X = H, F, Cl, \text{ or } Br$).³⁸ Otherwise, it would be tempting to link a weak C-H bond in CH_3SF_3 to the facility of HF elimination in accordance with the following scheme:^{11,41}



With the dimethyl derivative $(CH_3)_2SF_2$, the susceptibility to HF elimination is such that the compound cannot be vaporized without decomposition.^{11,42}

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Electronic Structure of Asymmetric Metal-Metal Multiple Bonds: The d^2 - d^6 Complexes $X_4Mo-Mo(PH_3)_4$ ($X = OH, Cl$)

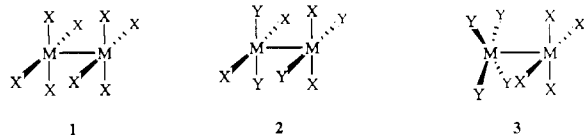
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The electronic structure of compounds containing the Mo_2^{4+} dimeric unit with a formally asymmetric $Mo(0)$ - $Mo(IV)$ charge distribution is investigated with the SCF- $X\alpha$ -SW method. Such systems are known for mixed phosphine-alkoxide ligand systems. Strong π -donor ligands such as the alkoxides inhibit the formation of a polar δ bond between the two metal centers and lead to a sterically induced staggered ligand conformation. These complexes contain a formal $Mo-Mo$ triple bond. Weaker π -donor ligands such as halides permit the δ charge transfer to occur and should lead to a stable, eclipsed ligand conformation with a net $Mo-Mo$ quadruple bond. Comparisons are made to the electronic structure of more conventional $Mo(II)$ - $Mo(II)$ dimers, particularly those with bidentate phosphine ligands and with a twisted ligand conformation about the dimetal unit.

The majority of complexes that contain multiple metal-metal bonds are homodinuclear molecules with symmetry-equivalent metal atoms. With reference to quadruple metal-metal bonds, the best studied systems are the d^4 - d^4 dimers of $Mo(II)$ or $Re(III)$.² The electronic structure of these d^4 - d^4 complexes is fairly well understood in terms of the "usual" quadruple-bond description: one σ metal-metal bond, two π metal-metal bonds, and one δ metal-metal bond, each of which is symmetrically disposed between the two metal atoms.

Most complexes with d^4 - d^4 quadruple bonds conform to two common coordination geometries, namely M_2X_8 systems with D_{4h} symmetry (1) or $M_2X_4Y_4$ complexes that are D_{2d} (2). The



eclipsed orientation of the ligands on each metal center, even when it would appear to be sterically unfavorable, is, of course, attributed

to the presence of the δ bond, which is sensitive to variations in the rotational angle between the two metal fragments. The eclipsed orientation maximizes the δ interaction and the metal-metal bonding.

The symmetry equivalence of the two metal centers is removed in the heterodinuclear complexes that are based on $Cr(II)$ - $Mo(II)$ or $Mo(II)$ - $W(II)$ dinuclear fragments.³ These lower symmetry systems do not demonstrate any significant chemical or spectroscopic differences from the homodinuclear ones, however; apparently the differences between the two metal centers are not great enough to induce a sizably different electronic structure, and they are best considered as "slightly polarized" d^4 - d^4 systems.⁴

Recent efforts have yielded truly asymmetric homodinuclear complexes, wherein the two metal atoms are in different formal oxidation states. Cotton, Walton, and co-workers have found that certain $Re(III)$ - $Re(III)$ dimers can disproportionate to give formal d^3 - d^5 $Re(IV)$ - $Re(II)$ dimers such as the C_{2v} molecules

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