virtually 0 and, therefore, variations in ϕ should have almost no effect on the antiferromagnetic coupling. (iii) For intermediate values of τ, ϵ^2 decreases very rapidly as τ increases. Consequently, for increasing τ values, the effect of ϕ is expected to become progressively less important and τ assumes the leading role. Finally, it may be noticed that eq 2 predicts the presence of a triplet ground state ($2J > 0$) for a τ angle near 50° or larger. The calculations lead to a similar expectation since Δ^2, and hence J_{AF}, turns out to be 0 for $\tau \sim 50°$ and ϕ in the range 101–105°. Although no complexes of type III or IV have been reported with $\tau \geq 50°$, it might be of some interest that $[Ph_4P]CuCl_3$,[27] $[Ph_4As]CuCl_3$,[28] $[Ph_4Sb]CuCl_3$,[29] $[Ph_4P]CuBr_3$,[30] and $[Ph_4As]CuBr_3$[31] exhibit τ angles in the range 45–50° and all have a triplet ground state.[30–32]

In conclusion, although it would be inappropriate to ascribe much significance to the actual computed τ and ϕ angles since they are dependent on the choice of parameters, the trends that emerge from the calculations are in agreement with the experimental results and provide a reasonable basis for a qualitative understanding of the relative merit of the τ and ϕ parameters in determining the extent of magnetic coupling in doubly bridged, nonplanar copper(II) dimers.

Registry No. $Cu_2L_2Cl_2$, 21448-43-1.

Supplementary Material Available: Listings of thermal parameters and hydrogen atom coordinates (2 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Gas-Phase Molecular Structure of Ethynylsulfur Pentafluoride, $F_5SC{\equiv}CH$, by Electron Diffraction

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Six-coordinate sulfur compounds of the types F_5SX and $(F_5S)_2Y$ have structural interest arising from the effect of the odd ligands on the relative lengths of the axial and equatorial S–F bonds and on the bond angles in the SF_5 groups. There are experimental structural data for the molecules with X = Cl,[3,4] Br,[5] F_2N,[6] OCN,[7] F_3C,[8,9] and FO[10] and for those with Y = HN,[11] FN,[11] and O.[12] Ab initio calculations (double-ζ or lower quality) for X = Cl have been done;[4] others involving polarization functions are in progress.[13] For the molecules with the ligands Br, FO, and OCN it was not possible to determine which of the S–F bond types was longer nor whether the F_a–S–F_e angle was different from 90°. For the molecules with the ligands F_2N, HN, FN, and O, the axial S–F bond was determined to be longer than the equatorial one and, except for F_5SNF_2 (where it was measured to be 90.0 (9)°), the F_a–S–F_e angles were found to be slightly less than 90°. In the case of F_5SCl the two types of S–F bonds were found to be insignificantly different, but the F_a–S–F_e angle at 89.63 (10)° is surely less than 90°. It is only for F_5SCF_3 that the axial bond is found to be shorter than the equatorial one (by 0.010 (7) Å), and in this case, too, the F_a–S–F_e angle at 89.5 (2)° appears to be slightly less than 90°. These data are summarized in Table I.

Table I. Values of Parameters for the SF_5 Group in F_5SX and $(F_5S)_2Y$ Molecules[a]

substituent		parameter			
X	Y	$\langle r(S{-}F)\rangle$	$\Delta r(S{-}F)$	$\angle F_a{-}S{-}F_e$	ref
F		1.5623 (4)	0.0	90.0	26
Cl[b]		1.5702 (10)	0.001 (8)	89.63 (10)	4
Br[c]		1.5970 (25)	0.0[d]	88.8[d]	5
F_2N		1.549 (4)	0.014 (27)[e]	90.0 (9)	6
OCN		1.567 (2)	0.0[d]	90.0[d]	7
C≡CH		1.574 (2)	0.001 (14)	88.9 (2)	this work
F_3C		1.570 (2)	−0.010 (7)	89.5 (2)	9
FO		1.530 (10)	0.0[d]	90.0[d]	10
	HN	1.568 (3)	0.015 (26)[e]	88.4 (5)	11
	FN	1.557 (4)	0.026 (28)[e]	88.1 (9)	11
	O	1.560 (4)	0.014 (42)[e]	87.9 (9)	12

[a] Distances (r) in angstroms, angles (∠) in degrees. If not otherwise noted, distances refer to r_a and angles to $\angle_a$. [b] Joint electron diffraction and microwave spectroscopic analysis; r_g distances and $\angle_\alpha$ angle. [c] From microwave spectroscopy. [d] Value fixed during structure refinement. [e] Error limit not reported. Value estimated from $\epsilon(\Delta r(S{-}F)) = \epsilon(r(S{-}F_e)) + \epsilon(r(S{-}F_a))$.

An interesting additional example of this type of molecule is ethynylsulfur pentafluoride, $F_5SC{\equiv}CH$. The interest lies in the combined effect of the spatial and electron-donating properties of the acetylenic group on the structure of the SF_5 group. In view of what had been found for the molecules discussed above, distortions of this group were expected to be small and difficult to measure accurately by electron diffraction. However, the prospects for success clearly would be improved if data at high scattering angles, which increases the resolution of some of the interatomic distances, were obtained. We decided to carry out an investigation that included high-angle data. After our work was well along, we learned that a parallel study of $F_5SC{\equiv}CH$ was also being carried out in Professor H. Oberhammer's laboratory;[14] we understand publication of that work is also planned.

Experimental Section

Preparation of F_5SC_2H. A 118-mmol amount of F_5SBr and 104 mmol of HC≡CH were placed in a 300-mL Hoke stainless steel vessel equipped with a Whitey stainless steel valve. The reaction mixture was heated at 57 ± 2 °C for 2.5 h. The $F_5SCH{=}CHBr$ adduct was distilled, and the fraction boiling at 80–91 °C was collected, washed with water, dried over $MgSO_4$ (12 h), and redistilled. The fraction boiling at 86–89 °C was collected in 45% yield for subsequent dehydrobromination.

The $F_5SCH{=}CHBr$ was dehydrobrominated according to a literature method.[15] $F_5SC{\equiv}CH$ was purified by trap-to-trap distillation using traps cooled to −78, −98, and −196 °C. The pure product was found in the −98 and −196 °C traps; yield 50%. The infrared spectrum agreed with the literature spectrum,[15] and the molecular weight was found to be 151.4 g/mol (theoretical value 152.1 g/mol).

Conditions of Experiments. The electron diffraction data were obtained with the Oregon State apparatus. Conditions of the experiments

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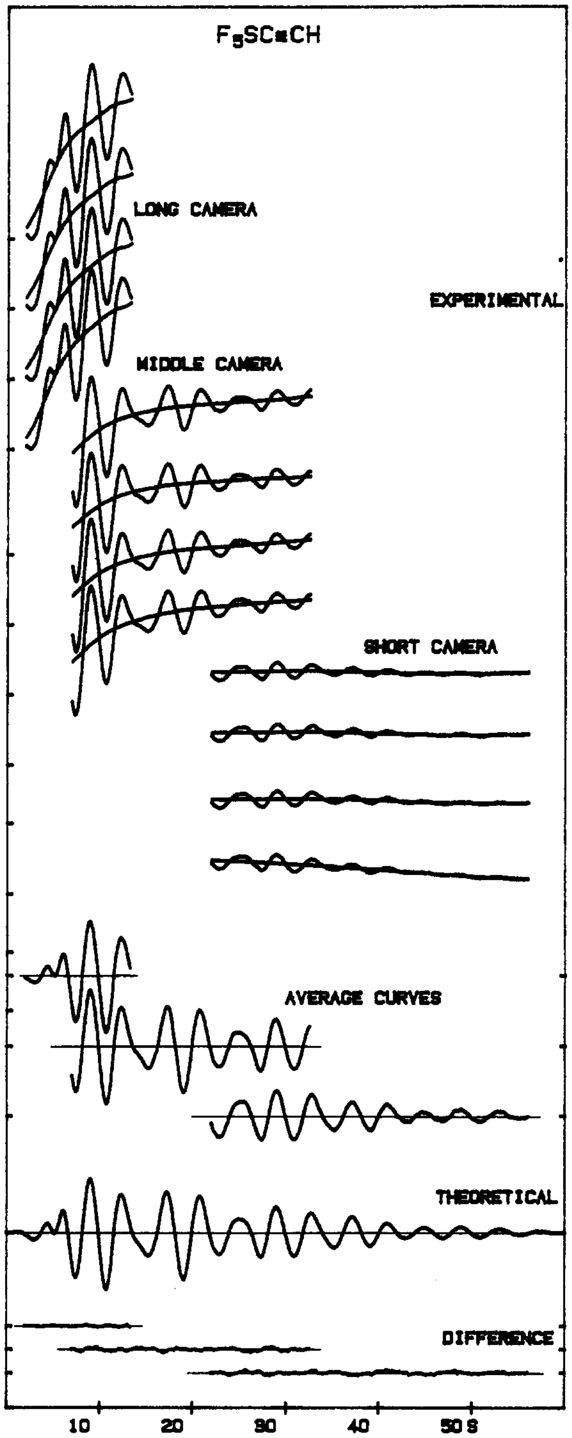

Figure 1. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 7 times relative to the backgrounds. The average curves are the molecular intensities $sI_m(s)$. The theoretical curve is for model A of Table II. Difference curves are experimental minus theoretical.

were as follows: sector shape, r^3; plates, 8 in. × 10 in. medium-contrast Kodak projector slide; development, 10 min in D-19 diluted 1:1; nominal nozzle-to-plate distances, 750 mm (long camera), 300 mm (middle camera), and 120 mm (short camera); nominal electron wavelength, 0.058 Å (calibrated in separate experiments with CO_2: $r_a(C{=}O) = 1.1646$ Å and $r_a(O{\cdot}O) = 2.3244$ Å); exposure times, 100–390 s; beam currents, 0.3–0.4 μA; ambient apparatus pressure during experiments, $(3–4) \times 10^{-6}$ torr; nozzle temperature, 19–20 °C; bath temperature, −67 °C.

Four plates from each camera distance were selected for analysis. The ranges of intensity data were $2.00 \le s/\text{Å}^{-1} \le 13.25$ (long camera), $7.00 \le s/\text{Å}^{-1} \le 32.50$ (middle camera), and $22.50 \le s/\text{Å}^{-1} \le 56.00$ (short camera); the data interval was $\Delta s = 0.25$ Å^{-1}. Procedures used for obtaining the total scattered intensities $(s_4I_t(s))$ and molecular intensities $(sI_m(s))$ have been described elsewhere.[16,17] Curves of the intensity data superimposed on their computer-generated backgrounds are shown in Figure 1. The data are available as supplementary material.

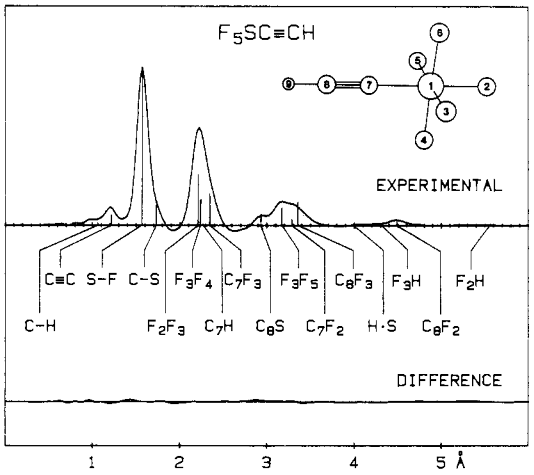

Figure 2. Experimental radial distribution curve. The lines denoting the interatomic distances have lengths proportional to the weights of the terms. The difference curve is experimental minus theoretical. The convergence coefficient B was given the value 0.000 75 Å^2.

Figure 2 shows the experimental radial distribution $(rD(r))$ of distances calculated in the usual way[16b] from the modified molecular intensity $I'(s) = s(I_m(s))Z_SZ_FA_S^{-1}A_F^{-1}\exp(-0.00075s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron-scattering amplitude.[18] The scattering amplitudes and phases were taken from tables.[18] The assignment of the interatomic distances is indicated by the vertical bars; they have lengths proportional to the weights of the terms.

Quadratic Force Field. We elected to carry out the structure refinement on r_α type distances, which required calculation of corrections for the effects of vibrational averaging. The distance conversions are given by $r_a = r_\alpha + \delta r + K - l^2/r = r_g - l^2/r$, where the centrifugal distortions δr and the perpendicular amplitude corrections K may be calculated from an appropriate vibrational force field and the root-mean-square amplitudes of vibration l are either calculated from the force field or obtained from the experiment.

It is known from experience, and from high-quality ab initio force field calculations,[19] that neither frequencies nor force constants can be transferred between structurally similar molecules with the precision required for spectroscopic work. However, the vibrational corrections required for the distance conversions in electron diffraction work are usually not very sensitive to changes in force field. Since there apparently exists no report of a gas-phase vibrational spectrum for $F_5SC{\equiv}CH$, we made use of this circumstance to generate a force field for it by combining quadratic force constants for the $-C{\equiv}CH$ part of $HC{\equiv}CH$[20] with those for the F_5SC part of F_5SCF_3.[9] The vibrational corrections δr and K as well as the amplitudes l calculated from this force field are found in Table II. To check the assumption of the insensitivity of these quantities to the force field, we repeated the process with use of the rather different force constants found for the F_5S part of F_5SCl.[3] The calculated quantities were nearly identical with those in Table II.

Structure Analysis. A diagram of the $F_5SC{\equiv}CH$ molecule is shown in Figure 2. With assumption of C_{4v} symmetry, six geometrical parameters are required to define the structure. For convenience these were chosen to be the distances $\langle r(S{-}F)\rangle = [4r(S{-}F_e) + r(S{-}F_a)]/5$, $\Delta r(S{-}F) = r(S{-}F_a) - r(S{-}F_e)$, $r(S{-}C)$, $r(C{\equiv}C)$, $r(C{-}H)$, and the bond angle $\angle(F_a{-}S{-}F_e)$. There are also 17 vibrational amplitude parameters. Because our diffraction data extended to high scattering angles, it was necessary to take cognizance of the effects of anharmonicity on the scattered intensity. Anharmonicity coefficients (κ) were calculated from $\kappa = al^4/6$, where a, the Morse anharmonicity constant, was given the value 1.8 Å^{-1} for S—F bonds,[3] 1.9 Å^{-1} for the S—C bond,[21] 2.0 Å^{-1}

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Table II. Structural Results for Models of $F_5SC{\equiv}CH$[a,b]

	model A[c]					model B[d]		model C[e]	
parameters	r_α, $\angle_\alpha$	r_g[f]	r_a[f]	l	l_{calcd}	r_α, $\angle_\alpha$	l	r_α, $\angle_\alpha$	l
$\langle r(S{-}F)\rangle$	1.574 (2)					1.574 (2)		1.574 (2)	
$\Delta r(S{-}F)$	0.002 (14)					0.002 (13)		[−0.010]	
$r(S{-}C)$	1.727 (5)					1.732 (6)		1.728 (5)	
$r(C{\equiv}C)$	1.202 (4)					1.193 (5)		1.203 (4)	
$r(C{-}H)$	[1.064]					[1.064]		[1.064]	
$\angle F_a{-}S{-}F_e$	88.9 (2)					88.9 (2)		89.0 (1)	
C—H	[1.064]	[1.081]	[1.076]	0.070 } (4)	0.074	[1.064]	0.074 } (8)	[1.064]	0.070 } (4)
C≡C	1.202 (4)	1.207	1.207	0.032 }	0.036	1.193 (5)	0.036 }	1.203 (4)	0.032 }
$S{-}F_e$	1.573 (3)	1.575	1.574	0.047 } (2)	0.043	1.574 (3)	0.048 } (2)	1.576 } (2)	0.047 } (2)
$S{-}F_a$	1.575 (11)	1.577	1.576	0.047 }	0.043	1.576 (10)	0.048 }	1.566 }	0.047 }
S—C	1.727 (5)	1.729	1.728	0.049 (5)	0.048	1.732 (6)	0.057 (7)	1.728 (5)	0.048 (5)
$F_2{\cdot}F_3$	2.205 (5)	2.207	2.206	0.063 } (3)	0.061	2.205 (5)	0.064 } (3)	2.202 (3)	0.063 } (3)
$F_3{\cdot}F_4$	2.225 (5)	2.227	2.225	0.064 }	0.062	2.225 (4)	0.065 }	2.228 (2)	0.064 }
$C_7{\cdot}H$	2.266 (5)	2.280	2.277	[0.079]	0.079	2.257 (6)	[0.079]	2.267 (5)	[0.079]
$C_7{\cdot}F_3$	2.358 (5)	2.360	2.358	0.071 (5)	0.069	2.362 (5)	0.073 (6)	2.359 (5)	0.071 (5)
$C_8{\cdot}S$	2.930 (7)	2.932	2.931	0.061 (10)	0.051	2.924 (7)	0.054 (9)	2.931 (6)	0.062 (10)
$F_3{\cdot}F_5$	3.146 (7)	3.148	3.146	0.062 (6)	0.054	3.146 (6)	0.063 (7)	3.151 (3)	0.063 (7)
$C_7{\cdot}F_2$	3.302 (12)	3.304	3.301	0.084 } (10)	0.059	3.307 (11)	0.087 } (10)	3.294 (6)	0.084 } (11)
$C_8{\cdot}F_3$	3.351 (6)	3.354	3.350	0.111 }	0.086	3.347 (7)	0.114 }	3.352 (6)	0.111 }
S·H	3.994 (7)	4.001	3.999	0.10 (18)	0.086	3.988 (8)	0.11 (17)	3.995 (7)	0.10 (17)
$F_3{\cdot}H$	4.320 (7)	4.327	4.323	0.127 } (25)	0.123	4.315 (7)	0.125 } (24)	4.320 (7)	0.126 } (24)
$C_8{\cdot}F_2$	4.504 (12)	4.505	4.505	0.065 }	0.061	4.500 (11)	0.063 }	4.498 (7)	0.064 }
$F_2{\cdot}H$	5.568 (12)	5.573	5.571	[0.092]	0.092	5.564 (11)	[0.092]	5.561 (8)	[0.092]
R[g]	0.053					0.031		0.054	

[a] Distances (r) and amplitudes (l) in angstroms and angles (∠) in degrees. Quantities in parentheses are estimated 2σ. For definitions see text. [b] The first six parameters were used to define the geometry. [c] Preferred model; based on data from long-, middle-, and short-camera experiments. [d] Based on data from long- and middle-camera experiments only. [e] Based on data from long, middle, and short cameras; $\Delta(S{-}F)$ constrained. [f] Uncertainties estimated to be the same as for r_α. [g] $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_i(\text{obsd})^2]^{1/2}$, where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Table III. Correlation Matrix (×100) for Parameters of Model A[a]

parameter	σ[b]	r_1	r_2	r_3	r_4	$\angle_5$	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}
1. $\langle r(S{-}F)\rangle$	0.02	100	1	28	1	−28	18	−45	8	3	8	14	−2	<1	−5	9
2. $\Delta r(S{-}F)$	0.49		100	−23	−12	−68	−23	1	−22	4	−1	34	11	−1	12	−5
3. $r(S{-}C)$	0.18			100	−17	31	59	−17	16	7	4	19	−9	−1	−11	13
4. $r(C{\equiv}C)$	0.14				100	3	−11	3	6	1	<1	−11	−12	−2	−13	−1
5. $\angle(F_a{-}S{-}F_e)$	5.34					100	17	12	13	−4	−1	−19	−4	<1	−8	4
6. $l(S{-}F_e;S{-}F_a)$	0.03						100	−8	13	5	8	24	−4	<1	−5	14
7. $l(S{-}C)$	0.16							100	−4	−2	<1	−16	−1	−1	<1	−10
8. $l(S{\cdot}C)$	0.35								100	−5	2	−2	−9	−1	−31	5
9. $l(S{\cdot}H)$	6.45									100	<1	7	−3	−2	2	1
10. $l(C{\equiv}C;C{-}H)$	0.13										100	<1	<1	−1	−2	<1
11. $l(F_2{\cdot}F_3;F_3{\cdot}F_4)$	0.05											100	2	<1	6	56
12. $l(C_7{\cdot}F_2;C_8{\cdot}F_3)$	0.35												100	<1	38	−2
13. $l(C_8{\cdot}F_2;F_3{\cdot}H)$	0.87													100	−1	<1
14. $l(F_3{\cdot}F_5)$	0.21														100	−3
15. $l(C_7{\cdot}F_3)$	0.16															100

[a] Distances (r) and amplitudes (l) in angstroms and angle (∠) in degrees. For numbering of atoms see Figure 1. For explanation of grouping of amplitudes see text. [b] Standard deviations from least squares.

for the C—H bond,[21] 1.6 Å^{-1} for the C≡C bond, and zero for all nonbonded distances.

Refinements of the r_α type structure were carried out by least squares,[22] with a theoretical $sI_m(s)$ curve adjusted simultaneously to three sets of experimental data comprising averages of the data from the several plates obtained at each nozzle-to-plate distance. A unit weight matrix was used. With use of either of the force fields mentioned above, the difference between $l(S{-}F_a)$ and $l(S{-}F_e)$ was calculated to be very small (less than 0.001 Å); accordingly, we restricted them to the same value for the structure refinements. The amplitudes for each of the distance pairs C≡C and C—H, $F_2{\cdot}F_3$ and $F_3{\cdot}F_4$, $C_8{\cdots}F_3$ and $C_7{\cdots}F_2$, and $C_8{\cdots}F_2$ and $F_3{\cdots}H$ were handled as single parameters by keeping their differences at the calculated values after tests indicated that the geometrical parameters were insensitive to small changes in these differences. Tests also indicated that $r(C{-}H)$ obtained an unreasonably small value (0.999 Å), and in the final refinements it was kept at 1.064 Å (r_α), the value in acetylene.[23] The argument in support of this choice is that the stretching frequencies are nearly the same: 3338 cm^{-1} for $F_5SC{\equiv}CH$[15] and 3374 and 3289 cm^{-1} for acetylene.[23] Similar tests showed that the amplitudes for the nonbonded distances between the hydrogen atom and those atoms on the symmetry axis of the molecule could not be refined. These amplitudes were given the calculated values.

Table II contains results for three models. The parameter sets refined in models A and B are identical, but the results for model B were obtained with omission of the short-camera data. The reason for the investigation of model B was to determine whether the results from the smaller data range would differ enough from those of the larger to affect our structural conclusions. Model C was designed to reveal whether an axial S—F distance slightly shorter than the equatorial ones was inconsistent with our data. Our preferred model is A. Table III is the correlation matrix for this model, and curves for it are shown in Figures 1 and 2.

Discussion

Our results for the structure of $F_5SC{\equiv}CH$ reveal nothing unusual. As is seen in Table I, the average S—F bond length is similar to that of several of the substituted sulfur hexafluorides, and in common with most of these the $F_a{-}S{-}F_e$ angle is slightly smaller than 90°. So far as the average distance is concerned, increasing length tends to be correlated with decreasing substituent-group electronegativity.[24,25] For example, shorter dis-

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tances are found in the molecules with the substituents F (sulfur hexafluoride itself[26]), F_2N, and FO and longer ones in molecules with the substituents Cl, Br, and C≡CH. The shortest distance is found for the substituent FO, which has the highest group electronegativity. The more electronegative substituents lead to the highest positive charge densities on the sulfur atom and thus to larger Coulombic attractions between it and the ligands. When a fluorine atom is replaced by a less electronegative atom or group, such as Cl, Br, O, CF_3, HN, and C≡CH, the charge density on sulfur lessens and the bonds to the fluorines correspondingly increase in length. (The group F_2N appears to be an exception; it leads to a decrease in average S—F bond length.) The above discussion concerns inductive effects, and a question may be asked about evidence for possible electron delocalization from the C≡CH group. The C≡C distance in our molecule, for which we estimate $r_\alpha^0 \simeq r_e$, is very nearly the same as in acetylene[23] (r_e = 1.2031 (5) Å), and the average S—F distance is similar to those in other molecules in which electron delocalization would not be expected. There is a great deal of variability in the lengths of S—C bonds in S^{VI} compounds. At 1.727 (5) Å in our molecule it is very much shorter than the 1.887 (8) Å found in F_5SCF_3[9] and somewhat shorter than the 1.771 (4) Å found in $O_2S(CH_3)_2$.[27] Since sp hybridization at carbon leads to bonds about 0.07 Å shorter than the sum of tetrahedral covalent single-bond radii, and since the Pauling tetrahedral radii for sulfur and carbon sum to 1.81 Å, we regard our S—C distance as normal. All in all, these distance comparisons indicate that there is very little electron delocalization in $F_5SC{\equiv}CH$.

The angle values in $F_5SC{\equiv}CH$ also have a simple interpretation. The widely successful VSEPR theory[28] calls for greater repulsion between the S—F_e bonds and the bond to groups less electronegative than the fluorine atom than between the S—F_a and S—F_e bonds. The consequence is $\angle F_a\text{-}S\text{-}F_e < 90°$. A similar angle deformation is to be expected from a balancing of steric interaction between the small axial and equatorial fluorine atoms, on the one hand, with that between the equatorial fluorines and the bulkier substituents on the other.

The important question of the relative lengths of the two types of S–F bonds in $F_5SC{\equiv}CH$ is unfortunately not resolved. Our preferred model A shows their lengths to be the same to within the uncertainty of the measurement. Moreover, as is seen from the results for model B in Table II, this result is independent of the exclusion of the high-angle data from our short-camera experiments. Model C provides a test. When the equatorial S—F bond is set and held at a value 0.010 Å longer than the axial one, the quality of fit is virtually identical with that obtained with model A and, as tests showed, is as good as when this bond is made the shorter one by the same amount. We conclude that the relative lengths of the two kinds of S—F bonds cannot be determined from electron diffraction data alone, even though, as ours do, they extend to much larger than the usual scattering angles. A similar situation was encountered in the case of F_5SCl[3,4] and was eventually resolved by an analysis[4] that incorporated rotational constants for several isotopic species. It seemed less likely that rotational constant data would be of help in the case of our symmetric-top molecule because there are several more structural parameters to which the rotational constant is very sensitive. We checked the matter as follows. First, the rotational constant B_z for our preferred model A was calculated. Its value was then successively changed by ±5 and ±10 MHz and the structure refined with these four B_z's used as constraints. The only parameter that obtained values beyond the range of uncertainty listed for it in model A was r(C—S); even so, its values lay in the narrow range $1.720\ (5) \le r(\text{C—S})/\text{Å} \le 1.734\ (4)$. Corresponding results for the S—F bond length difference were $-0.003\ (6) \le \Delta r(\text{S—F})/\text{Å} \le 0.005\ (6)$. We conclude it is not possible to determine which of the two types of S—F bonds is longer to within the uncertainty given for it in model A.

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Registry No. F_5SC_2H, 917-89-5; HC≡CH, 74-86-2; F_5SBr, 15607-89-3; $F_5SCH{=}CHBr$, 58636-82-1.

Supplementary Material Available: Total intensities (Table IV), final backgrounds (Table V), and molecular intensities (Table VI) from each plate (18 pages). Ordering information is given on any current masthead page.

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Thermodynamic Study of Lanthanide Complexes of 1,4,7-Triazacyclononane-*N*,*N*′,*N*″-triacetic Acid and 1,4,7,10-Tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic Acid

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Current interest in the complexation properties of lanthanide selective reagents has led to the synthesis of many new macrocycles derived from cyclic polyaza and cyclic polyaza polyoxa ligands with a wide variety of ionizable functional groups.[1-5] The thermodynamics of lanthanide complexation with these ligands should depend upon internal cavity size,[6] rigidity, and nature of the donating atoms.

Although there has been much interest in design of new lanthanide selective ligands, there have been few studies of the thermodynamic stability of such complexes.[7-10] We have been interested in using lanthanide complexes of macrocyclic polyaza polyacetate ligands as aqueous NMR shift reagents and MRI contrast agents.[11,12] As some of these ligands form complexes too slowly with the lanthanides for thermodynamic measurements to be made by the usual potentiometric methods, we have developed a spectrophotometric technique that allows the determination of stability constants over a wide range of values. The thermodynamic stability constants for the lanthanide complexes of 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid (NOTA) and 1,4,7,10-tetraazacyclodedecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (DOTA) are reported in this work.

Experimental Section

Reagents. The ligands NOTA and DOTA were synthesized by methods reported previously.[11,13] Arsenazo III (99.99%), purchased from Aldrich Chemical Co., was used without further purification. Solutions of the lanthanides were prepared from the trichloride salts and were standardized by titration with EDTA with xylenol orange used as the indicator.

Spectrophotometric Titrations. The lanthanide and Arsenazo III solutions were buffered at pH 3.89 with 0.01 M acetate buffer at an ionic strength of 0.1 (NaCl). Conditional stability constants for the 1:1 and 1:2 complexes[14] of the lanthanides with Arsenazo III were determined by titrating a standard lanthanide solution directly in a 1.00-cm cuvette with a standard Arsenazo III solution while the absorbance was monitored at 660 nm. Free Arsenazo III absorbs only slightly at this wavelength and pH (ϵ = 650 L/(mol cm)) while the 1:1 and 1:2 lanthanide complexes of Arsenazo III have extinction coefficients of 35 000 and 50 000 l/(mol cm), respectively. Titrant was added to the cuvette so that the lanthanide:Arsenazo III ratio varied between 3:1 and 1:1.7.

The conditional stability constants of the lanthanides with NOTA and DOTA were measured by titrating a solution of the lanthanide–Arsenazo III mixture, containing a mixture of 1:1 and 1:2 complexes, with the desired ligand. As it took several days for the macrocycle–lanthanide–Arsenazo III mixtures to reach equilibrium at the low concentrations used in this work, it became expedient to maintain the solutions at 60 °C in a sealed cuvette for 12–18 h followed by an additional 6–10-h room-

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