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Molecular Structure and Quadratic Force Field of Chromyl Fluoride, CrO_2F_2

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The molecular structure of chromyl fluoride has been reinvestigated at room temperature by electron diffraction from the gas. With use of vibrational data from the work of others, a quadratic force field has been determined. The geometry of the molecule (distances *r* and angles ∠) and the amplitudes of vibration (*l*), with parenthesized uncertainties estimated as 2σ, are given by the parameter values $r_g(\mathrm{Cr{=}O}) = 1.575\ (2)$ Å, $r_g(\mathrm{Cr{-}F}) = 1.720\ (2)$ Å, $r_g(\mathrm{O{\cdot}O}) = 2.543\ (14)$ Å, $r_g(\mathrm{O{\cdot}F}) = 2.685\ (4)$ Å, $r_g(\mathrm{F{\cdot}F}) = 2.846\ (15)$ Å, $\angle_\alpha\mathrm{OCrO} = 107.8\ (8)°$, $\angle_\alpha\mathrm{FCrF} = 111.9\ (9)°$, $\angle_\alpha\mathrm{OCrF} = 109.3(2)°$, $l(\mathrm{Cr{=}O}) = 0.045\ (2)$ Å, $l(\mathrm{Cr{-}F}) = 0.048\ (2)$ Å, $l(\mathrm{O{\cdot}O}) = 0.079\ (17)$ Å, $l(\mathrm{O{\cdot}F}) = 0.087\ (8)$ Å, and $l(\mathrm{F{\cdot}F}) = 0.098\ (22)$ Å; allowance for the effects of vibrational averaging ("shrinkage") is included. The values of the symmetrized force constants (based on C_{2v} symmetry for the molecule) are found to be similar to, and consistent with, those found previously for chromyl chloride. The structure is discussed.

Introduction

A recent article from this laboratory reported the results of a reinvestigation of the molecular structure of gaseous chromyl chloride[2] by electron diffraction. The work was undertaken primarily to check the values of the OCrO and ClCrCl bond angles obtained in an early investigation,[3] according to which the former is the smaller by several degrees, in disagreement with valence-shell electron-pair repulsion (VSEPR) theory.[4] The newer results for this molecule are much more precise than the older ones, but otherwise agree well with them.

The structure of chromyl fluoride, CrO_2F_2, appears also to be "abnormal" in the same sense as CrO_2Cl_2; i.e., the FCrF bond angle measured from electron diffraction[5] was found to be 118.91 (46)°—larger than the value 102.14 (36)° found for the OCrO angle. Although the sign and magnitude of this angle difference agree with an interpretation of the gas-phase Raman and matrix-isolated IR spectra,[6] the difference is remarkable by comparison with CrO_2Cl_2 ($\angle$ClCrCl = 113.3 (3)°, $\angle$OCrO = 108.5 (4)°) and seemed to us likely to be in error. For example, the sizes and bonding properties of oxygen and fluorine atoms are much more similar than those of oxygen and chlorine, suggesting smaller deviations of all bond angles from the tetrahedral value in CrO_2F_2 than in CrO_2Cl_2. An additional uncertainty about the CrO_2F_2 structure arises from an interpretation of the microwave spectrum,[7] which has the OCrO angle larger than the FCrF angle in disagreement with both the electron diffraction and vibrational spectroscopic results.

The uncertainties just described have led us to undertake a reinvestigation of the CrO_2F_2 structure by electron diffraction. As part of the analysis we needed to evaluate a quadratic force field for the molecule, a calculation that does not appear to have been done heretofore. This article reports the results of our structure and normal-coordinate analyses.

Table I. Experimental Conditions

	long camera	intermed camera	short camera
nozzle-to-plate distance/mm	744.79	301.04	121.37
exposure time/s	45–60	120	300–360
beam current/μA	3.9–4.1	3.0–3.1	5.7–5.8
ambient apparatus press./torr × 10^6	4.4–4.8	4.3–6.0	5.1–6.3
no. of plates used	4	4	2
ranges of data/*s*	2.00–12.25	6.00–30.00	25.00–48.00
data interval/*s*	0.25	0.25	0.25

Table II. Values of Symmetry Force Constants for CrO_2F_2[a,b]

A_1	F_{11}(CrO)	7.811 (63)	0.569 (102)	[0][d]	[0][d]
	F_{22}(CrF)		4.933 (39)	[0][d]	[0][d]
	F_{33}(OCrO)[c]			1.050 (15)	[0][d]
	F_{44}(FCrF)[c]				0.440 (11)
A_2	F_{55}(OCrF)[c]	0.607			
B_1	F_{66}(CrO)	7.129 (46)	0.401 (63)		
	F_{77}(OCrF)[c]		0.706 (8)		
B_2	F_{88}(CrF)	4.559 (22)	0.070 (21)		
	F_{99}(OCrF)[c]		0.734 (4)		

[a] Units are aJ/Å^2 for stretches, aJ/rad^2 for bends, and aJ/(Å rad) for stretch-bend interactions. [b] Uncertainties are σ. [c] These symmetry coordinates involve other angles as well. The main contribution is from the angle which is listed. [d] Assumed.

Experimental Section

The sample of CrO_2F_2 was prepared (G.L.G. and B.M.J.) according to procedures previously described.[8] The diffraction experiments (R.J.F., L.H., and K.H.) were carried out with the Oregon State apparatus using an r^3 sector. The 8 × 10 in. Kodak projector slide plates (medium contrast) were developed for 10 min in D-19 developer diluted 1:1. The sample bath temperature was kept at −11 to −18 °C, and the nozzle was at room temperature. Other experimental conditions are summarized in Table I. The methods for extracting the intensity data from the plates, the calculation of intensity and radial distribution curves, and the sources of the electron scattering factors and phases were essentially as described for CrO_2Cl_2.[2] Anharmonicity constants κ for use in the intensity calculations were estimated to be 0.61×10^{-6} and 0.89×10^{-6} Å^3 for the Cr=O and Cr—F bonds, respectively, and were set equal to zero for the nonbond distances. The coefficient *B* in the convergence factor used in radial distribution calculations was given the value 0.0005 Å^2. The experimental intensity curves are shown in Figure 1 superimposed on their backgrounds; the final radial distribution curve is shown in Figure 2.

Quadratic Force Field

Vibrational infrared spectra of CrO_2F_2 have been reported for the gas[9] and for matrix-isolated samples;[6] Raman spectra have been reported for the gas,[6] liquid,[10] and solid.[10] Some of the assignments by Hobbs[9] have been revised by Stammreich et al.,[11] and although a few of these have been questioned,[10] they appear to be correct.[6] We used Hobbs's data with the assignments of Stammreich et al. and the

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(1) (a) Oregon State University. (b) Portland State University.

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(9) Hobbs, W. E. *J. Chem. Phys.* **1958**, *28*, 1220.

(10) Brown, S. D.; Gard, G. L.; Loehr, T. M. *J. Chem. Phys.* **1976**, *64*, 1219.

(11) Stammreich, H.; Kawai, K.; Tavares, Y. *Spectrochim. Acta* **1959**, *15*, 438.

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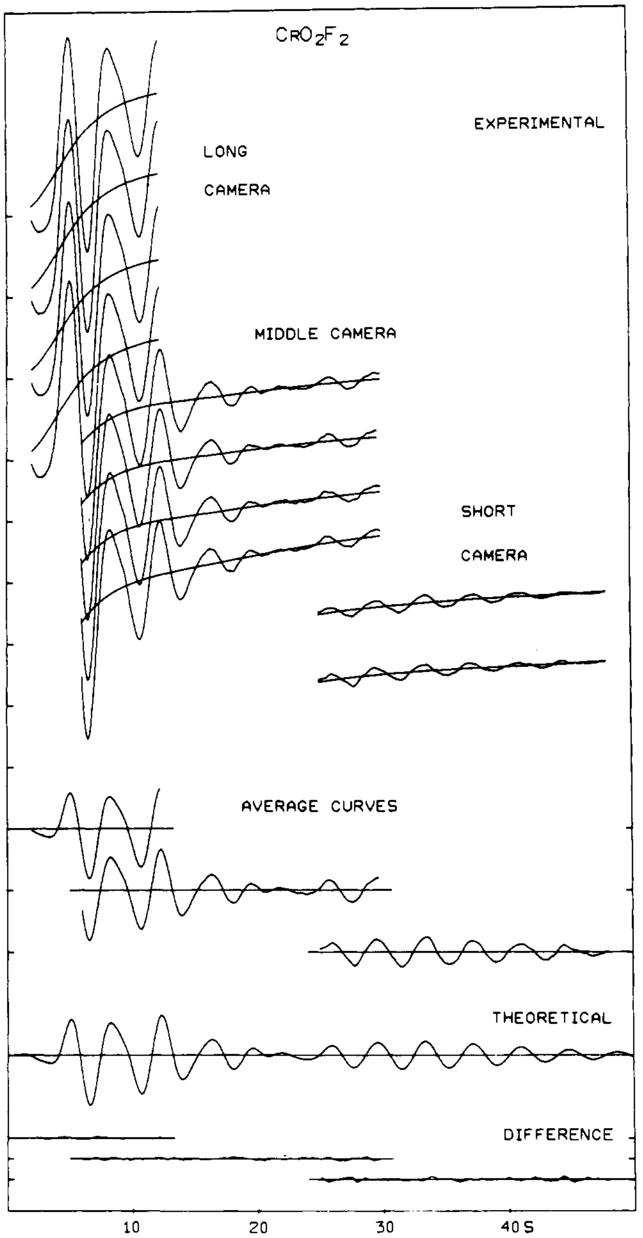

Figure 1. Intensity curves. The experimental curves are s^4I_T shown superimposed on the calculated backgrounds. The curves are magnified 7.5 times relative to the backgrounds. The average molecular intensity curves are in the form sI_m. The theoretical curve corresponds to the model from this work found in Table V. The difference curves are experimental minus theoretical.

wavenumber shifts measured for several chromium isotopes by Beattie et al.[6] together with our molecular structure in the force field calculations. The symmetry coordinates for the C_{2v} molecule were those of Shimanouchi and Suzuki.[12] The data are not sufficient to determine values for all off-diagonal constants in the a_1 block, and several of these were arbitrarily set to zero. The resulting force constants are given in Table II. The wavenumbers and isotopic shifts calculated from our force field are in excellent agreement with those observed. These quantities as well as the force constant correlation matrix are given in the supplementary material.

Structure Analysis

A CrO_2F_2 molecule of C_{2v} symmetry has five different interatomic distances, which are specified by the values of four structural parameters. A convenient set is $\langle r_\alpha \rangle = [r_\alpha(CrF) + r_\alpha(CrO)]/2$, $\Delta r_\alpha = r_\alpha(CrF) - r_\alpha(CrO)$, $\langle \angle_\alpha \rangle = [\angle_\alpha FCrF + \angle_\alpha OCrO]/2$, and $\Delta\angle_\alpha = \angle_\alpha FCrF - \angle_\alpha OCrO$. The geometrically consistent set of r_α distances generated by these parameters was converted to the r_a set applicable to the scattering equations in fashion similar to that used for CrO_2Cl_2; the perpendicular amplitude corrections were calculated from the force field of Table II, and the mean-square amplitudes were those determined from the structure refinements.

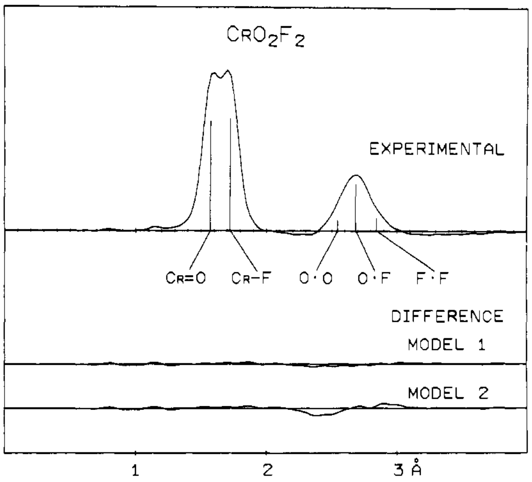

Figure 2. Experimental radial distribution curve calculated from a composite of the average molecular intensity curves of Figure 1 after adding data from the theoretical curve for $s < 2.00$ and multiplying by $Z_{Cr}Z_F/A_{Cr}A_F$. The convergence coefficient B was 0.0005 $Å^2$. The difference curves are experimental minus theoretical; model 1 corresponds to the distance distribution shown and model 2 has the O·O and F·F distances approximately exchanged.

The radial distribution curve for CrO_2F_2 has a barely resolved peak corresponding to the two bond distances in the molecule, and a single, broad peak corresponding to the three different nonbond distances. It is reasonable to place the O·F distance near the center of the second peak, but the relative locations of the O·O and F·F distances are not obvious. Accordingly, we tested two trial structures differing in the values of the OCrO and FCrF angles in such a way as to approximately exchange the locations of the O·O and F·F distances. The refinements were done by least squares in the usual way, fitting a theoretical intensity curve simultaneously to three sets of experimental data comprising the averaged intensities from the plates made at each camera distance. In the case of the model with $r(O·O) < r(F·F)$ (model 1), we were able to refine simultaneously and independently the four structural parameters and the five vibrational amplitudes corresponding to all distances. For model 2, however, which has $r(O·O) > r(F·F)$, the refinement was much less stable and failed to converge without introduction of severe limitations such as restriction of all nonbond amplitudes to the calculated values obtained from our force field and a model 2 geometry. Since all attempts to refine the nonbond amplitudes for model 2 led eventually to model 1, and since the quality of fit provided by forcing convergence to models of the second type was very much poorer than that from model 1 (as is seen in Figure 2), we eliminated model 2 from further consideration. The final results are summarized in Table III. Table IV is the corresponding correlation matrix.

Discussion

The results of our structure analysis of CrO_2F_2 differ in important respects from those obtained in the previous electron diffraction study.[5] There are also differences between our angle values and those predicted from the analysis of the vibrational spectrum[6] and between our structure and the rotational constants from the microwave investigation.[7] As may be seen from Table III, the diffraction investigation by Garner et al. (GMD) led to nonbond distances spread out over a much larger range than ours. Since GMD's report contains no radial distribution curve nor, unfortunately, any values for the vibrational amplitudes, the reasons for the disagreement are not clear. We did investigate the fit of these authors' model to our data, however, first by calculating a radial distribution curve for their model (we assumed reasonable values for the amplitudes) and second by refining the nonbond amplitudes

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[12] Shimanouchi, T.; Suzuki, I. *J. Mol. Spectrosc.* **1962**, *8*, 222. The redundant coordinate coefficient *c* in this article was multiplied by $^1/_2$.

Table III. Structural Results for CrO_2F_2[a,b]

parameter	r_α or $\angle_\alpha$[c]	r_g	r_a	l	l_{calcd}[d]	r or $\angle$ (GMD)[e]
Cr=O	1.572 (2)	1.575 (2)	1.574 (2)	0.045 (2)	0.037	1.579 (4)
Cr–F	1.716 (2)	1.720 (2)	1.719 (2)	0.048 (2)	0.041	1.739 (4)
O·O	2.540 (14)	2.543 (14)	2.541 (14)	0.079 (17)	0.071	2.456
O·F	2.682 (4)	2.685 (4)	2.682 (4)	0.087 (8)	0.081	2.696
F·F	2.844 (15)	2.846 (15)	2.843 (15)	0.098 (22)	0.097	2.995
∠OCrO	107.8 (8)					102.1 (4)
∠FCrF	111.9 (9)					118.9 (5)
∠OCrF	109.3 (2)					108.6
R^f	0.053					0.117

[a] Distances (r) and amplitudes (l) in angstroms; angles in degrees. For definition of distance types see ref 1. [b] Parenthesized values are estimated 2σ uncertainties. [c] Values of parameters used to define structure are $\langle r_\alpha \rangle = 1.644$ (2), $\Delta r_\alpha = 0.145$ (1), $\langle \angle_\alpha \rangle = 109.9$ (4), and $\Delta \angle_\alpha = 4.0$ (16). [d] Calculated from force field of Table III. [e] Garner, Mather, and Dove.[4] [f] $R = \Sigma_i w_i \Delta_i^2 / \Sigma_i [s_i I_i(\text{obsd})]^2$, $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table IV. Correlation Matrix (×100) for Structure Parameters of CrO_2F_2

parameter	σ_{LS}[a]	r_1	r_2	r_3	r_4	r_5	$\angle_1$	$\angle_2$	$\angle_3$	l_1	l_2	l_3	l_4	l_5
r(CrO)	0.00032	100	38	14	19	12	4	8	−14	−7	−35	−4	−1	5
r(CrF)	0.00033		100	15	19	13	11	3	−16	38	5	2	6	7
r(O·O)	0.0049			100	−24	−61	99	−64	−31	<1	−4	59	69	42
r(O·F)	0.0011				100	−48	−26	−50	92	4	−10	−16	8	35
r(F·F)	0.0053					100	−63	99	−54	7	2	−40	−66	−62
∠OCrO	0.30						100	−65	−30	<1	<1	60	69	42
∠FCrF	0.31							100	−53	3	2	−40	−67	−63
∠OCrF	0.065								100	−4	−2	−16	7	32
l(CrO)	0.00031									100	44	4	6	4
l(CrF)	0.00030										100	12	8	2
l(O·O)	0.0059											100	80	57
l(O·F)	0.0024												100	78
l(F·F)	0.0077													100

[a] Standard deviation not including estimates of correlation or systematic effects. Distances and amplitudes are given in angstroms and angles are in degrees.

Table V. Bond Lengths and Bond Angles for Some MO_2X_2 Molecules[a]

parameter	CrO_2F_2[b]	CrO_2Cl_2[c]	SO_2F_2[d]	SO_2Cl_2[e]	SeO_2F_2[d]
r(M=O)	1.574 (2)	1.580 (2)	1.397 (2)	1.417 (3)	1.575 (2)
r(M–X)	1.719 (2)	2.124 (2)	1.530 (2)	2.011 (4)	1.685 (2)
r(O·O)	2.541 (14)	2.562 (8)	2.450 (14)	2.492 (6)	2.809 (8)
r(O·X)	2.682 (4)	3.023 (4)	2.378 (4)	2.792 (6)	2.637 (3)
r(X·X)	2.843 (15)	3.544 (7)	2.286 (20)	3.085 (7)	2.467 (10)
∠OMO	107.8 (8)	108.5 (4)	122.6 (12)	123.5 (2)	126.2 (5)
∠XMX	111.9 (9)	113.3 (3)	96.7 (11)	100.3 (2)	94.1 (5)
∠OMX	109.3 (2)	108.7 (1)	108.6 (2)	108.0 (1)	108.0 (1)

[a] Distances (r_a) in angstroms; angles in degrees. [b] This work. [c] Reference 1. [d] Hagen, K.; Cross, V. R.; Hedberg, K. *J. Mol. Struct.* **1978**, *44*, 187. [e] Hargittai, M.; Hargittai, I. *Ibid.* **1981**, *73*, 253. Numbers calculated from r_g in this reference.

on the basis of their geometry. The calculated radial distribution curve shows a partial resolution of the three nonbond distances incompatible with the appearance of our experimental peak at 2.7 Å, and the refinement attempt led to unreasonable, even bizarre, values for the amplitudes. These tests together with the better value for the quality-of-fit factor R for our structure lead us to conclude that GMD's results, where they differ substantially from ours, are in error. The angle values derived by Beattie et al.[6] (BMO) from isotopic shifts of certain stretching vibrations are 102.5° (OCrO) and 124° (FCrF) with estimated uncertainties of about 10°. The OCrO angle is thus in fair agreement with ours, but the FCrF angle is too large. It is likely that the error in this FCrF value stems from the assumption of separability of the high- and low frequency vibrations, which is a poorer approximation in the case of the Cr—F stretches than the Cr═O. The microwave values for the rotational constants[7] are A_0 = 4410.0 MHz, B_0 = 4286.9 MHz, and C_0 = 4235.2 MHz. The corresponding values from our r_α structure are 4443.2, 3933.7, and 3636.8 MHz. Although small differences between the two sets are to be expected because of the effects of thermal vibrational averaging contained in the electron diffraction values, these large differences cannot be reconciled. We believe the microwave values for B and C to be incorrect.

The character of the bonds in the CrO_2F_2 molecule may be inferred as follows. The Pauling radius R_1 for chromium and Schomaker–Stevenson radius for fluorine together with correction for electronegativity difference[13] lead to the prediction 1.71 Å for the length of a Cr—F single bond. The length of a Cr═O double bond is predicted to be 1.56 Å by subtracting 0.21 Å, the usual difference between single- and double-bond lengths, from the single-bond radius sum obtained in a similar way. These predictions are very close to the observed values and accordingly we may regard the Cr—F and Cr═O links as essentially pure single and double bonds. Similar calculations in the case of CrO_2Cl_2 led to the same conclusion for its two bond types,[2] and since the bond angles are also very similar, it may be concluded that the bonding at the chromium atoms does not differ in any important way in the two molecules. There is some uncertainty about the use of the radius R_1 for this calculation since it was derived from empirical considerations based on distances measured in the metal and in intermetallic compounds. A larger value for the chromium

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(13) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapters 7 and 11.

radius would imply higher multiplicity for all bonds, but the conclusions about the similarity of the bonding in CrO_2F_2 and CrO_2Cl_2 would remain.

According to VSEPR theory, the amount of space in the coordination sphere of an atom occupied by single, double, and triple bonds to that atom increases with increasing bond multiplicity. Application of this and a few other simple postulates of the theory has led to successful predictions of the relative magnitudes of bond angles in a wide variety of substances among which are the sulfuryl and selenyl halides whose structures are summarized in Table V. As is seen from the table, however, the theory fails for the chromyl halides, where the angle between the bonds to the oxygen atoms is found to be slightly smaller than that between the halogen bonds. This angle relationship is also found in several other pairs of similar molecules that differ in having a main-group vs. a transition-metal atom at the central position.

The angle differences just mentioned, though puzzling, are no more so than some other structural features of the group 6 molecules revealed in Table V. For example, the OMX angles are remarkably similar in all five cases. Also, the O·O distances for the sulfur and chromium compounds differ by at most about 0.12 Å, despite the large differences in the M=O bond lengths and OMO bond angles. We see no simple model of the bonding which successfully rationalizes all features of the structures in Table V. In respect to the difference between the FMF angles in SO_2F_2 and CrO_2F_2, however, both GMD[5] and BMO[6] have noted that Coulomb repulsion between the fluorine atoms should be greater in the latter than in the former because their atomic charges are larger in the latter. BMO have also pointed out that the FCrF angle bending constant is smaller than the FSF constant and that the observed relative values for ∠FMF in the two compounds are consistent with a balancing of these repulsions and angle strains.

Our values for the symmetrized force constants for CrO_2F_2 are similar to those found in CrO_2Cl_2[2,14] for all modes except those comprising primarily Cr—X bond stretches. For these modes the Cr—F constants, while still in the single-bond range, are nearly twice the magnitude of the corresponding Cr—Cl ones, a difference similar to that observed for fluorine and chlorine bonded to other atoms. The consistency of the force fields for these two molecules supports the conclusion obtained from comparison of the bond lengths that the bonding in them is similar. Finally, we note that BMO[6] have obtained values for the internal stretching and stretch–stretch interaction constants that differ only very slightly from those derived from our symmetry force field. The values in aJ/Å^2 (BMO in parentheses) are f(CrO) = 7.470 (7.429), f(CrF) = 4.746 (4.774), f(CrO,CrO) = 0.341 (0.382), f(CrF,CrF) = 0.187 (0.384), and f(CrO,CrF) = 0.284 (0.390). The differences may be attributed to the different structures used in the normal-coordinate analyses.

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Registry No. CrO_2F_2, 7788-96-7.

Supplementary Material Available: Tables of vibrational wavenumbers and isotopic shifts, the force constant correlation matrix, total scattered intensities, calculated backgrounds, and average molecular intensities from the three camera distances (14 pages). Ordering information is given on any current masthead page.

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(14) Varetti, E. L.; Müller, A. *Spectrochim. Acta, Part A* **1978**, *34A*, 895.

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Photoelectron Spectroscopic and Theoretical Study of Tris(trimethylsilyl)amine and Related Silylamines. Real and Hypothetical Planar Tertiary Amines

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The lowest ionization potential (IP), corresponding to ionization of a nitrogen 2p "lone-pair" orbital, was studied experimentally via photoelectron spectroscopy (PES) and theoretically by using semiempirical (MNDO) and ab initio methods, in the three series $(CH_3)_{3-n}N(SiH_3)_n$, $(CH_3)_{3-n}N(Si(CH_3)_3)_n$, and $(CH_3CH_2CH_2)_{3-n}N(Si(CH_3)_3)_n$, n = 0–3. The ab initio calculations on $(CH_3)_2NSiH_3$ predict a very flat potential surface around nitrogen, suggesting a balance of forces tending toward pyramidal and planar geometries. The results do not wholly support a previous interpretation of electron diffraction data for this molecule. The question of d-orbital participation in the Si–N bond is discussed in terms of an effect on the geometry of the silylamines and an effect on the IP's of the silylamines. A method of extrapolating measured IP's to arrive at the vertical IP of a (hypothetical) planar tertiary amine has been presented. For planar trimethylamine a vertical IP of 7.7–7.9 eV is predicted. For planar tri-*n*-propylamine the vertical IP is predicted to be 7.4 eV. MNDO calculations on tri-*tert*-butylamine suggest that the reason for its nonexistence is entirely steric, not electronic.

Introduction

Tris(trimethylsilyl)amine is an intriguing compound for at least two reasons. First, it is quite remarkable that three extremely bulky trimethylsilyl groups can "fit" around one nitrogen while three *tert*-butyl groups cannot, or, at least, have not yet been made to fit.[1] Second, tris(trimethylsilyl)amine is fascinating because it is an aliphatic amine that is planar, whereas other amines are pyramidal.

We have undertaken a photoelectron spectroscopic (PES) and theoretical study of tris(trimethylsilyl)amine and related silylamines, the results of which we report herein.

Experimental Section

Except for *N*,*N*-bis(trimethylsilyl)propylamine and *N*-(trimethylsilyl)di-*n*-propylamine, all compounds were commercial samples (Petrarch Systems, Inc.) whose purity was checked by H NMR. The two compounds mentioned above were synthesized by literature

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(1) Methyldi-*tert*-butylamine has recently been synthesized: Audeh, C. A.; Fuller, S. E.; Hutchinson, R. J.; Lindsay-Smith, J. R. *J. Chem. Res., Miniprint* **1979**, 2984.

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