range from C(24)-H(24) = 0.79 (7) Å through C(17)-H(17) = 1.04 (6) Å. The average value is 0.90 Å (rms scatter = 0.070 Å; σ(of mean) = 0.013 Å). This value is contracted from the accepted internuclear C-H distance of ~1.08 Å[30] due to the asphericity of the electron density about the bonded hydrogen atom[31] and is lower than the value of ~0.95 Å normally found from X-ray diffraction studies,[32] probably as a result of librational shortening due to the rigid-body motion of the phenyl groups (*vide supra*).

(3) The external hydrogen-carbon-carbon angles of the phenyl groups are each expected to be ~120°. The most asymmetrically situated hydrogen atom is H(5), which is involved in the angles H(5)-C(5)-C(4) = 132 (5)° and H(5)-C(5)-C(6) = 107 (5)°. However each of these angles varies by only ~2.5σ from its expected value. All other H-C-C angles lie in the range 112 (6)-128 (6)° and no other angle varies from the idealized value of ~120° by more than 1.4σ.

(4) The coplanarity of hydrogen atoms with carbon atoms of the phenyl groups may be examined in Table V. The largest deviations from planarity are (in order) 0.18 Å (or ~2.6σ) for H(24), 0.14 Å (or ~2.3σ) for H(15), and 0.11 Å (or ~1.6σ) for H(27). All other hydrogen atoms are within 0.10 Å (or ~1.5σ) of the appropriate carbocyclic plane.

Finally, it should be emphasized that the above summary demonstrates that the positions of the refined hydrogen atoms are (within the limits of experimental error) entirely consistent with chemical expectations. Observed deviations of individual hydrogen atoms from the locations predicted by assuming idealized pseudo-D_{6h} geometry of the phenyl rings are of no statistical significance.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1065.

[30] *Chem. Soc., Spec. Publ.*, No. 18, S18s-S19s (1965).

[31] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[32] M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

Contribution from Bell Laboratories,
Murray Hill, New Jersey 07974

Crystal Structure of Iodine Pentafluoride at −80°

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Iodine pentafluoride, IF_5, is monoclinic: $a = 15.07$ (2) Å, $b = 6.836$ (10) Å, $c = 18.24$ (2) Å, $\beta = 92.96$ (14)°, most probable space group $C2/c$, 20 molecules per unit cell, and 2.5 molecules in the asymmetric unit. The intensities were measured by the stationary-crystal technique using a scintillation counter. The structure was refined by least squares to $R = 0.064$, $R_w = 0.049$. Although there are individual variations among the three crystallographically distinct molecules, they appear to be chemically equivalent with the distorted tetragonal-pyramidal shape to be expected from the Gillespie–Nyholm valence shell electron pair repulsion theory. The molecular dimensions (weighted average over all molecules) are I-F_{apical} = 1.75 (3) Å, I-F_{basal} = 1.87 (3) Å, and F_{apical}-I-F_{basal} = 81.9 (4)°. The pattern of polar contacts between molecules forms an extended three-dimensional array which fills space. The structure is of interest because the IF_5 molecule is isoelectronic with the XeF_5^+ ion.

Introduction

IF_5 in the crystalline state was studied more than 20 years ago by photographic techniques.[1] The unit cell is monoclinic with most probable space group symmetry of Cc or $C2/c$. Assuming 20 molecules per unit cell and a calculated density of ~3.9 g cm^{-3} implies that the asymmetric unit contains either 5 or 2.5 molecules depending on the space group. In either event the structure appeared complex for the techniques available at the time and the analysis was not completed.

The recent analysis of the cubic XeF_6 structure[2,3] has created renewed interest in the IF_5 structure because the IF_5 molecule is isoelectronic with the XeF_5^+ ion. In the known crystalline phases of XeF_6 the molecules are always dissociated into XeF_5^+ and F^- ions.[2,4] The valence electron lone pair is sterically active and the XeF_5^+ ion has the shape of a distorted tetragonal pyramid as expected by the Gillespie–Nyholm theory.[5,6] The XeF_5^+ ions are bridged by F^- ions to form tetrameric or hexameric rings of nearly spherical overall shape. The bridging F^- ions make angles of about 35° with the Xe-lone pair axis.

One would expect the IF_5 molecule to have the same shape as the XeF_5^+ ion. Then the question arises as to whether it is possible for the molecules to be oriented in

[1] R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, 27, 982 (1957).

[2] R. D. Burbank and G. R. Jones, *Science*, 168, 248 (1970).

[3] R. D. Burbank and G. R. Jones, *J. Amer. Chem. Soc.*, 96, 43 (1974).

[4] R. D. Burbank and G. R. Jones, *Science*, 171, 485 (1971).

[5] R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11, 339 (1957).

[6] R. J. Gillespie, *J. Chem. Educ.*, 40, 295 (1963).

Table I. Final Positional and Thermal Parameters (Standard Deviations in Parentheses)

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I1	0	0.25496 (42)	$^1/_4$	0.00116 (8)	0.01130 (57)	0.00207 (9)	0	−0.00009 (6)	0
I2	0.10678 (9)	0.69298 (27)	0.05351 (9)	0.00223 (7)	0.01277 (57)	0.00172 (6)	−0.00027 (13)	−0.00002 (5)	−0.00027 (14)
I3	0.21479 (9)	0.68555 (25)	0.34574 (9)	0.00127 (6)	0.01114 (46)	0.00169 (6)	−0.00032 (13)	0.00003 (5)	0.00008 (15)
F1	0	0.0074 (36)	$^1/_4$	0.0028 (9)	0.0206 (60)	0.0025 (8)	0	0.0005 (7)	0
F2	0.1020 (8)	0.2134 (20)	0.1990 (8)	0.0024 (6)	0.0265 (53)	0.0031 (6)	−0.0005 (15)	0.0008 (5)	−0.0034 (17)
F3	0.0683 (8)	0.2158 (17)	0.3371 (8)	0.0048 (8)	0.0094 (48)	0.0023 (6)	0.0006 (14)	−0.0019 (5)	0.0033 (13)
F4	0.0614 (9)	0.9107 (21)	0.0869 (9)	0.0063 (10)	0.0091 (41)	0.0046 (8)	0.0064 (17)	0.0004 (7)	−0.0029 (18)
F5	0.0015 (9)	0.7042 (19)	−0.0092 (7)	0.0040 (7)	0.0251 (53)	0.0002 (4)	0.0029 (16)	−0.0008 (4)	0.0017 (15)
F6	0.1612 (8)	0.8634 (25)	−0.0072 (8)	0.0035 (7)	0.0256 (48)	0.0028 (6)	−0.0015 (17)	0.0004 (5)	−0.0001 (18)
F7	0.1980 (8)	0.7518 (22)	0.1237 (7)	0.0028 (7)	0.0347 (57)	0.0024 (6)	−0.0057 (18)	−0.0002 (5)	−0.0009 (20)
F8	0.0415 (9)	0.5819 (24)	0.1289 (7)	0.0047 (9)	0.0299 (60)	0.0016 (6)	−0.0023 (17)	0.0002 (6)	−0.0047 (16)
F9	0.1329 (8)	0.8478 (19)	0.3769 (7)	0.0029 (7)	0.0086 (34)	0.0023 (5)	0.0042 (13)	0.0002 (5)	−0.0001 (14)
F10	0.1197 (7)	0.6020 (21)	0.2829 (7)	0.0026 (7)	0.0172 (42)	0.0019 (5)	−0.0049 (14)	−0.0013 (5)	0.0012 (14)
F11	0.2288 (8)	0.8819 (22)	0.2801 (7)	0.0026 (7)	0.0142 (40)	0.0027 (6)	−0.0034 (14)	−0.0003 (5)	0.0002 (15)
F12	0.2875 (8)	0.8229 (23)	0.4155 (8)	0.0037 (8)	0.0380 (64)	0.0024 (7)	−0.0056 (18)	0.0003 (5)	−0.0069 (18)
F13	0.1740 (8)	0.5336 (21)	0.4214 (7)	0.0030 (7)	0.0242 (52)	0.0019 (5)	−0.0045 (15)	0.0008 (5)	−0.0031 (16)

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

such a fashion that intermolecular polar attractions are possible.

Experimental Section

The apparatus and general techniques for low temperature control and X-ray measurement are identical with those used in the cubic XeF_6 study.[3] The IF_5 was heat sealed in a 0.5-mm diameter capillary of fluorinated ethylene-propylene copolymer.

In general we have found that liquid to solid transformations are much more difficult to handle than vapor to solid transformations. In the latter case well-formed single crystals often occur that are well separated from their neighbors, are firmly attached to the capillary wall, and can be readily isolated in the X-ray beam (so that diffraction is occurring from only one crystal). In liquid to solid crystal growth considerable manipulation and control of the cold gas stream is required with attendant visual observation in the polarizing microscope. The crystals do not have a well-defined shape and often the crystallographic orientations that occur most frequently are not convenient. It proved to be very time consuming to obtain satisfactory specimen crystals of IF_5.

Photographic and counter observations with Mo Kα, λ 0.7107 Å, confirmed that IF_5 is monoclinic with most probable space group symmetry of Cc or $C2/c$, *i.e.*, hkl reflections are present only if $h + k = 2n$, $h0l$ reflections are present only if $l = 2n$. The unit cell constants at −80° are $a = 15.07$ (2) Å, $b = 6.836$ (10) Å, $c = 18.24$ (2) Å, and $\beta = 92.96$ (14)°.

Intensity measurements were made with a manually operated single-crystal orienter with scintillation counter detection. The stationary-crystal technique was used with 10-sec counts at peak and at background on both sides of each peak. Counting rates were kept below 10,000 cps with a series of Zr filters of known attenuation. The crystal was oriented with the [201] direction along the φ axis. Reflections observable at $\chi = 90°$ did not vary by more than 3% in intensity as a function of φ so an empirical absorption correction as a function of φ was not obtained.

Reflections were considered to be observable if the intensity exceeded 3 times the standard error in the counting statistics. The number of unique reflections theoretically observable within a maximum scattering angle of $2\theta = 50°$ was 1650. At a point where 630 unique reflections had been observed by the above criteria, the experiment came to an end because of an unfortunate failure to replenish the liquid N_2 supply over a weekend period with a resultant loss of the crystal. The existing data included all the planes with spacings large enough to have higher orders within the sphere of reflection as well as measurements of the higher orders. Because these data gave a good approximation to a spherical distribution in reciprocal space and because of the difficulty experienced in growing suitable crystals it was decided to conduct the structure analysis with the restricted set of data. The restriction undoubtedly made it more difficult to obtain a trial model of the fluorine positions but did not prevent our obtaining the desired structural information. The data were corrected for the Lorentz and polarization effects but not for absorption before reduction to structure factors.

Structure Analysis

The computer programs used included FOUR,[7] ORFLS,[8] and ORFFE.[9] Space group $C2/c$ was assumed to be correct and this was borne out by the subsequent analysis. The positions of the I atoms were obtained from the Patterson synthesis. There are four I atoms in special position $0, y, {}^1/_4$ on twofold axes and sixteen I atoms in two sets of general x, y, z positions. The I positions were refined by least-squares analysis followed by a difference Fourier synthesis. In the least-squares procedure the quantity minimized was $\Sigma w(F_o - F_c)^2$ where w is a weighting factor derived from the counting statistics and F_o and F_c are the observed and calculated structure factors. The difference function contained about 3 times as many peaks as were required to account for the fluorine atoms. However, the atoms belonging to the molecules situated on the twofold axes could be identified with the assumption of the expected geometry of a distorted tetragonal pyramid and indicated an I-apex distance of ~1.70 Å, I-base distance of ~1.85 Å, and apex-I-base angle of ~80°. Assuming the remaining molecules would have similar dimensions, trial and error procedures were used

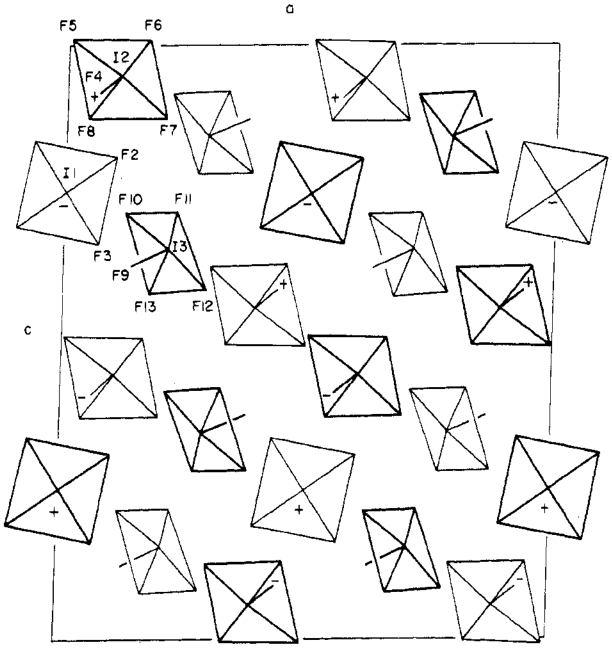

Figure 1. Contents of unit cell in projection along b axis. IF_5 tetragonal pyramids represented by skeletal outlines to preserve clarity. Light and heavy lines designate molecules situated at heights of roughly $^1/_4$ and $^3/_4$ along the b axis, respectively. Plus and minus signs used to indicate whether apex of I1 and I2 pyramids projects up or down.

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(7) P. B. Jamieson, Memorandum 68-1522-3, Bell Laboratories, Murray Hill, N. J., 1967.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

Table II. Interatomic Distances (Å) and Angles (deg) (Standard Deviations in Parentheses)

A. Within IF_5 Molecules

I1-F1	1.69 (2)	I2-F4	1.76 (1)	I3-F9	1.77 (1)
I1-F2	1.85 (1)	I2-F5	1.92 (1)	I3-F10	1.89 (1)
I1-F3	1.88 (1)	I2-F6	1.82 (1)	I3-F11	1.82 (1)
I1-F2$^{\mathrm{I}}$	1.85 (1)[a]	I2-F7	1.89 (1)	I3-F12	1.90 (1)
I1-F3$^{\mathrm{I}}$	1.88 (1)	I2-F8	1.88 (1)	I3-F13	1.85 (1)
F1-F2	2.31 (2)	F4-F5	2.40 (2)	F9-F10	2.40 (2)
F1-F3	2.34 (2)	F4-F6	2.35 (2)	F9-F11	2.33 (2)
F1-F2$^{\mathrm{I}}$	2.31 (2)	F4-F7	2.40 (2)	F9-F12	2.41 (2)
F1-F3$^{\mathrm{I}}$	2.34 (2)	F4-F8	2.40 (2)	F9-F13	2.37 (2)
F2-F3	2.59 (2)	F5-F6	2.64 (2)	F10-F11	2.52 (2)
F2-F2$^{\mathrm{I}}$	3.65 (2)	F5-F7	3.77 (2)	F10-F12	3.75 (2)
F2-F3$^{\mathrm{I}}$	2.63 (2)	F5-F8	2.70 (2)	F10-F13	2.67 (2)
F3-F2$^{\mathrm{I}}$	2.63 (2)	F6-F7	2.55 (2)	F11-F12	2.62 (2)
F3-F3$^{\mathrm{I}}$	3.72 (3)	F6-F8	3.67 (2)	F11-F13	3.63 (2)
F2$^{\mathrm{I}}$-F3$^{\mathrm{I}}$	2.59 (2)	F7-F8	2.63 (2)	F12-F13	2.62 (2)
F1-I1-F2	81.2 (4)	F4-I2-F5	81.3 (6)	F9-I3-F10	82.1 (6)
F1-I1-F3	81.8 (4)	F4-I2-F6	81.9 (7)	F9-I3-F11	81.3 (6)
F1-I1-F2$^{\mathrm{I}}$	81.2 (4)	F4-I2-F7	82.4 (7)	F9-I3-F12	82.3 (6)
F1-I1-F3$^{\mathrm{I}}$	81.8 (4)	F4-I2-F8	82.4 (7)	F9-I3-F13	81.8 (6)
F2-I1-F3	87.9 (6)	F5-I2-F6	89.6 (6)	F10-I3-F11	85.9 (6)
F3-I1-F2$^{\mathrm{I}}$	89.6 (6)	F6-I2-F7	86.7 (6)	F11-I3-F12	89.9 (6)
F2$^{\mathrm{I}}$-I1-F3$^{\mathrm{I}}$	87.9 (6)	F7-I2-F8	88.7 (6)	F12-I3-F13	88.7 (6)
F3$^{\mathrm{I}}$-I1-F2	89.6 (6)	F8-I2-F5	90.5 (5)	F13-I3-F10	91.0 (6)
F2-I1-F2$^{\mathrm{I}}$	162.3 (9)	F5-I2-F7	163.7 (6)	F10-I3-F12	164.3 (6)
F3-I1-F3$^{\mathrm{I}}$	163.6 (8)	F6-I2-F8	164.1 (7)	F11-I3-F13	163.0 (6)

B. Primary Polar Contacts between Molecules

I1-F10	3.03 (1)	F1-I1-F10	141.6 (3)
I1-F10$^{\mathrm{I}}$	3.03 (1)	F1-I1-F10$^{\mathrm{I}}$	141.6 (3)
I2-F12$^{\mathrm{III}}$	3.03 (1)	F4-I2-F12$^{\mathrm{III}}$	148.3 (6)
I2-F13$^{\mathrm{V}}$	3.07 (1)	F4-I2-F13$^{\mathrm{V}}$	147.6 (6)
I3-F2$^{\mathrm{II}}$	2.91 (1)	F9-I3-F2$^{\mathrm{II}}$	136.8 (5)

C. Secondary Polar Contacts between Molecules

I1-F8	3.22 (2)	F1-I1-F8	134.0 (3)
I1-F8$^{\mathrm{I}}$	3.22 (2)	F1-I1-F8$^{\mathrm{I}}$	134.0 (3)
I2-F5$^{\mathrm{VI}}$	3.25 (1)	F4-I2-F5$^{\mathrm{VI}}$	126.5 (5)
I3-F7$^{\mathrm{III}}$	3.28 (1)	F9-I3-F7$^{\mathrm{III}}$	142.3 (5)
I3-F11$^{\mathrm{III}}$	3.23 (2)	F9-I3-F11$^{\mathrm{III}}$	146.7 (5)

D. Intermolecular Fluorine Distances <4.0 Å

F2-F5$^{\mathrm{VI}}$	3.79 (2)	F5-F5$^{\mathrm{VI}}$	2.81 (3)	F7-F11$^{\mathrm{III}}$	3.25 (2)
F2-F10	3.02 (2)	F5-F8$^{\mathrm{VI}}$	2.99 (2)	F7-F12$^{\mathrm{II}}$	3.98 (2)
F2-F11$^{\mathrm{III}}$	2.81 (2)	F5-F9$^{\mathrm{I}}$	3.35 (2)	F7-F12$^{\mathrm{III}}$	3.03 (2)
F2-F12$^{\mathrm{III}}$	2.82 (2)	F5-F13$^{\mathrm{I}}$	3.35 (2)	F7-F13$^{\mathrm{II}}$	2.87 (2)
F3-F5$^{\mathrm{IV}}$	3.06 (2)	F5-F13$^{\mathrm{V}}$	3.35 (2)	F8-F9$^{\mathrm{I}}$	3.19 (2)
F3-F6$^{\mathrm{IV}}$	3.17 (2)	F6-F12$^{\mathrm{II}}$	3.63 (2)	F8-F10	3.01 (2)
F3-F7$^{\mathrm{III}}$	3.57 (2)	F6-F13$^{\mathrm{II}}$	3.11 (2)	F8-F10$^{\mathrm{I}}$	2.97 (2)
F3-F8$^{\mathrm{I}}$	3.07 (2)	F6-F13$^{\mathrm{V}}$	3.02 (2)	F8-F12$^{\mathrm{III}}$	3.25 (2)
F3-F10	2.93 (2)	F7-F9$^{\mathrm{III}}$	3.76 (2)	F8-F13$^{\mathrm{I}}$	3.36 (2)
F3-F11$^{\mathrm{III}}$	3.96 (2)	F7-F10	3.34 (2)	F10-F10$^{\mathrm{I}}$	3.76 (2)
F3-F13	3.07 (2)	F7-F10$^{\mathrm{II}}$	3.98 (2)	F10-F11$^{\mathrm{III}}$	3.00 (2)
F4-F9$^{\mathrm{I}}$	3.06 (2)	F7-F11	3.01 (2)	F11-F11$^{\mathrm{II}}$	3.65 (1)
F4-F12$^{\mathrm{II}}$	3.62 (2)				

[a] Roman numerals refer to atoms at symmetry-equivalent positions: I $= -x, y, {}^1/_2 - z$; II $= {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; III $= {}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$; IV $= x, 1 - y, {}^1/_2 + z$; V $= x, 1 - y, -{}^1/_2 + z$; VI $= -x, 1 - y, -z$.

with alternate sequences of least-squares and difference syntheses to locate the remaining fluorine atoms.

The fully identified model with 3 I atoms and 13 F atoms in the asymmetric unit was refined by least squares with isotropic thermal parameters to $R = 0.170$, $R_w = 0.148$, where $R = \Sigma|F_o - F_c|/\Sigma|F_o|$, $R_w = [\Sigma w(F_o - F_c)^2]^{1/2}/(\Sigma w F_o{}^2)^{1/2}$. There were sizable discrepancies for certain reflections which appeared to be of a systematic nature. Various empirical relations were sought as a function of φ, or χ, or 2θ and it was noted that a plot of F_o/F_c *vs.* $F_o/2\theta$ (deg) gave a roughly linear relation with negative slope. The F_o were corrected by multiplying by $0.893 + 0.0155F_o/2\theta$ (deg) which made F_o/F_c approximately constant as a function of $F_o/2\theta$. This we regarded as an empirical absorption correction. The corrected data were refined by anisotropic least-squares to $R = 0.064$, $R_w = 0.049$. The final positional and thermal parameters are listed in Table I. A comparison of F_o and F_c is available (see paragraph at end of paper regarding supplementary material).

Description of the Structure

The contents of the unit cell are illustrated in Figure 1. The intramolecular distances and angles for the three types of molecules in the asymmetric unit are summarized in Table II. Although there are individual variations among the three molecular types, they would appear to be chemically equivalent. The molecular dimensions (weighted average over all molecules) are illustrated in Figure 2. The molecular shape is clearly that to be expected from the Gillespie-Nyholm theory[5,6] with a sterically active valence electron lone pair on the I atom.

From the ESCA studies of Karlsson, *et al.*,[10] we assumed that in the $XeF_5{}^+$ ion[3] each F ligand carries a charge of 0.3− and the Xe atom carries a charge of 2.5+. One might expect a similar charge of 0.3− on each F ligand in the IF_5 molecule which implies a charge of 1.5+ on the I atom. One would therefore expect polar attractions to exist be-

(10) S. E. Karlsson, K. Siegbahn, and N. Bartlett, Report UCRL-18502, Lawrence Radiation Laboratory, Berkeley, Calif., 1969.

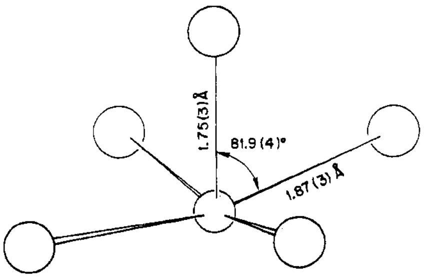

Figure 2. Iodine pentafluoride molecule. The dimensions are a weighted average over all three crystallographic types present in unit cell.

tween the ligands of neighboring molecules and the I atom of a given molecule. Such polar contacts do indeed exist in the IF_5 structure and the pertinent distances and angles are summarized in Table II. If it is assumed that the I-lone pair axis is directed in the opposite direction to the I-apex axis, then the angle between an attracted F atom and the lone pair axis is given by the supplement of the angle between the attracted F atom and the I-apex axis.

The polar contacts fall into two groups. The first which we call primary polar contacts have a weighted-average distance of 3.01 (6) Å and make a weighted-average angle of 36.4 (3.5)° with the I-lone pair axis. The secondary contacts have a weighted average distance of 3.25 (2) Å and a weighted-average angle of 42.6 (7.8)° with the I-lone pair axis. Given the shape of the molecules and their relative orientations in space the secondary contacts would appear to be merely a geometrical consequence of the formation of the primary contacts.

The environment around each crystallographic type of molecule is quite distinct. The I1 molecule makes primary contacts with four I3 molecules and secondary contacts with two I2 molecules. The I2 molecule makes primary contacts with two I3 molecules and secondary contacts with one I1, one I2, and one I3 molecule. The I3 molecule makes primary contacts with two I1 and two I2 molecules and secondary contacts with one I2 and two I3 molecules. The total pattern of primary contacts is sufficient to define the crystal structure as a single array extended throughout three-dimensional space.

Referring again to Figure 1, the extended array may be regarded as based on a distortion of face-centered cubic packing. If, for the moment, each molecule is regarded as a simple sphere, the $(\bar{2}04)$ and (402) planes are the most densely occupied planes in projection and indeed these planes give rise to the largest structure factors among the diffraction measurements. Each iodine atom has twelve iodine neighbors arranged approximately on a face-centered sublattice. The packing is quite compact as indicated by the intermolecular, nonpolar fluorine to fluorine distances in Table II.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or a microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1071.

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Metal-Centered Rearrangements of Zirconium β-Diketonates. Evidence for Twisting Modes of Activation

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Some key derivatives in a series of zirconium β-diketonates of the types $(h^5\text{-}C_5H_5)Zr(dik)_2Cl$ and $(h^5\text{-}C_5H_5)Zr(dik)_3$, along with an example of a new cationic species $(h^5\text{-}C_5H_5)Zr(dik)_2^+$, have been prepared, and their rates of metal-centered rearrangement have been determined by nmr methods. The labilities of the molecular compounds have been compared with those of related derivatives in which the pentahapto C_5H_5 group has been replaced by a halogen. Significant relationships between structure and lability exist which provide a basis for favoring twisting over bond-rupture modes of activation. The methyl proton line-broadening patterns associated with ligand interchange in $(h^5\text{-}C_5H_5)Zr(dpm)_2Cl$ and $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ (dpm = $(t\text{-}C_4H_9)COCHCO(t\text{-}C_4H_9)$ and acac = $CH_3COCHCOCH_3$) were analyzed in terms of specific twist mechanisms. Although the process is nonrandom, no simple, single-step facial twist mechanism operates. A reasonable combination of facial and digonal twists, however, is consistent with the observed line shapes.

It is generally recognized that metal chelates may undergo intramolecular rearrangements either by bond rupture processes in which one metal-chelate bond breaks to give an activated complex of reduced coordination number or by twisting processes in which the bonds rotate but do not open. Distinguishing between these two modes of activation is a challenging problem, as evidenced by the relatively few examples for which a mechanistic assignment has been possible.[1-3] Recently, dynamic nmr studies of the inversion of certain "fast" trigonal-antiprismatic tropolonates[4,5] and dithiocarbamates[6,7] have led to an incisive

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 4.

(2) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, 6, 331 (1971).

(3) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press.

(4) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972).

(5) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 95, 1116 (1973).

(6) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 11, 2843 (1972).