

TABLE I  
THEORETICAL RESULTS

Symmetry	Xe-F r	-E, e.v.	BE, e.v.	$\lambda$ , e.v., of highest MO's Occupied			
XeF <sub>2</sub> : D <sub>∞h</sub>	2.4	707.0	3.3	-11.3	-14.9	-14.9	
	C <sub>2v</sub> <sup>a</sup>	2.4	705.5	2.6	-12.1	-13.8	-14.9
	C <sub>4v</sub> <sup>a</sup>	2.4	704.0	1.8	-12.8	-13.0	-14.9
XeF <sub>4</sub> : D <sub>4h</sub>	1.7	975.5	-18.6	16.9	16.9	-11.3	
	1.9	1002.3	0.5	2.3	2.3	-13.0	
	2.1	1011.6	2.8	-5.5	-5.5	-14.0	
	2.4	1013.8	3.4	-11.2	-11.2	-14.8	
	2.8	1011.5	2.8	-14.1	-14.1	-15.1	
	C <sub>4v</sub> <sup>b</sup>	2.4	1007.7	1.9	-12.1	-12.3	-12.3
	C <sub>2v</sub> <sup>b</sup>	2.4	1009.6	2.4	-11.2	-12.8	-12.8
	T <sub>d</sub>	2.4	1007.4	1.8	-12.3	-12.3	-12.3

<sup>a</sup> Assumed bond angle of 120° for C<sub>2v</sub> and 90° for C<sub>2v</sub>'.

<sup>b</sup> Assumed bond angles of 70° 32' for C<sub>4v</sub> and 90° for C<sub>2v</sub>.

than 2 Å., the highest MO's in energy for each molecule (Table I) are those that consist primarily of xenon 5p orbitals, which span the irreducible representations  $a_{2u} + e_u$  in D<sub>4h</sub>,  $a_1 + e$  in C<sub>4v</sub>,  $a_1 + b_1 + b_2$  in C<sub>2v</sub>,  $t_2$  in T<sub>d</sub>, and  $\sigma_u + \pi_u$  in D<sub>∞h</sub>. As the two highest MO's are vacant in XeF<sub>4</sub>, T<sub>d</sub> symmetry does not correspond to a closed shell configuration. Now, as  $\lambda_e < \lambda_{a_1}$  in C<sub>4v</sub>, but  $\lambda_{a_{2u}} < \lambda_{e_u}$  in D<sub>4h</sub>, the latter symmetry corresponds to a closed-shell, while the former does not. For XeF<sub>2</sub> there is only one vacant MO, and as  $\lambda_{\pi_u} < \lambda_{\sigma_u}$ , a closed-shell configuration is found. The lower total orbital energy of XeF<sub>2</sub> with D<sub>∞h</sub> symmetry arises primarily from the relatively lower energy of the two occupied, antibonding  $\pi_u$  MO's consisting largely of xenon 5p orbitals perpendicular to the bond axis. Similarly, a D<sub>4h</sub> symmetry is favored for XeF<sub>4</sub> because of the lower energy of the occupied MO of  $a_{2u}$  symmetry consisting primarily of a xenon 5p orbital perpendicular to the molecular plane.

The bond energy for square-planar XeF<sub>4</sub> (Table I) is a maximum for a Xe-F distance of 2.4 Å., a value much larger than observed I-F distances of 1.7-1.9 Å. As a check on the energy minimum, an idealized C<sub>4v</sub> model of IF<sub>5</sub>, with all bond angles at 90° and with equal bond lengths, was considered, assuming iodine parameters equal to xenon parameters. The energy minimum was again found at 2.4 Å., a value which probably arises for XeF<sub>4</sub> from an overestimation of interactions involving the xenon 5s orbital (or possibly 5p orbitals). The results obtained for XeF<sub>5</sub> assuming no interactions involving the xenon 5s orbital give an energy minimum at approximately 2.1 Å., with a bond energy of 4.0 e.v. The justification of the neglect of nuclear repulsions and the overestimation of bond energies by an approximate factor of two will be discussed elsewhere.<sup>2</sup>

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## THE CRYSTAL AND MOLECULAR STRUCTURE OF XENON DIFLUORIDE BY NEUTRON DIFFRACTION

Sir:

As accurate molecular parameters for the new compounds of xenon<sup>1</sup> are of interest in clarifying the nature of their chemical binding, a neutron diffraction study of XeF<sub>2</sub> at room temperature has been undertaken. A sample furnished by D. F. Smith, who recently reported<sup>2</sup>

(1) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); C. L. Chernick, et al., *Science*, **138**, 136 (1962); N. Bartlett, *Proc. Chem. Soc.*, 218 (1962).

preparation and characterization of the compound, yielded several crystals when distilled into thin-walled vitreous silica capillaries; one having the shape of an irregular hexagonal platelet ( $\sim 1.5 \times 1.0 \times 0.5$  mm.), well separated from other crystals, was selected for neutron diffraction measurements. These were made on the Oak Ridge automatic neutron diffractometer<sup>3</sup> with a neutron wave length of 1.077 Å.

The tetragonal body-centered lattice indicated by preliminary X-ray precession photographs was confirmed by neutron measurements on 67 non-extinguished equivalent pairs of reflections ( $hkl, khl$ ) and at positions of 53 reflections required to be absent by body centering. Intensities for constant  $l$  index decreased monotonically with increasing scattering angle, and those for  $l = 0, 3, 4, 7$  and 10 were outstandingly strong; thus placement of Xe at the origin and F on tetrad axes at  $\pm (00z)$ ,  $z \approx 2/7$ , of space group I4/mmm is indicated. Absorption effects were indicated to be less than 1% by measurement of the transmission of neutrons through the 1 mm. dimension of the crystal. The specimen was found to undergo a steady growth, ascribed to sublimation from other crystals in the tube, during the 10 days of data collection. This necessitated a correction to the measured intensities to establish a consistent scale, based on periodic repetitions of the (020) reflection. The factors ranged from 1.38 to 0.807 and were judged accurate to better than 4%. Corresponding crystal weights, deduced from the final scale factor and the beam intensity, were 1.53 to 2.62 mg.

Refinement of the structure by iterative least squares from 334 intensity observations, of which 90 were symmetrically non-equivalent, using the computer program of Busing and Levy,<sup>4</sup> yielded the over-all scale factor and these parameters, listed with their standard errors appended in parentheses

	$s$	$\beta_{11}$	$\beta_{22}$	$f(10^{-13}$ cm)
Xe (0.0)	0.0323(17)	0.0078(5)	+0.462(9)	
F 0.2837(3)	0.0642(17)	0.0087(3)	(0.55, assumed)	

The reliability index  $\Sigma(F^2_{\text{obsd}} - F^2_{\text{calcd}})/\Sigma F^2_{\text{obsd}}$  reached 0.097.

The symmetric linear molecules are aligned on the tetrad axes with the Xe-F distance of 1.983 ( $\sigma = 0.002$ ) Å. The anisotropic thermal parameters suggest that the molecules undergo thermal displacements, of which the root mean square is described by a cone of precession about the symmetry axis with a half angle of about 7°; this distribution of the molecules implies that the observed Xe-F distance is foreshortened<sup>5</sup>; a corrected mean separation,<sup>6</sup> based on the assumption that F atoms "ride" on Xe, is 2.00 Å. ( $\sigma = 0.01$ ).

Each F atom has one F neighbor at 3.02 Å. and four at 3.08 Å. Eight non-bonded F neighbors coordinate each XeF<sub>2</sub> molecule at the vertices of a square prism at the distance 3.64 Å. from Xe.

The Xe-F bond distance of 2.00 Å. seems not inconsistent with the value 2.36 Å. found<sup>7</sup> in the pseudo-isoelectronic ion ICl<sub>2</sub><sup>-</sup>, if correction is made for the difference in radius of Cl and F, and qualitative allowance is made for the negative ionic charge. However, Smith<sup>2</sup> presents spectroscopic evidence that the type of binding is not similar.

(2) D. F. Smith, *J. Chem. Phys.*, in press.

(3) W. R. Busing and H. A. Levy, American Crystallographic Society, Boulder Meeting, 1961.

(4) W. R. Busing, K. O. Martin and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," Report No. TM-305, Oak Ridge National Laboratory.

(5) D. W. J. Cruickshank, *Acta Cryst.*, **14**, 754 (1956).

(6) W. R. Busing and H. A. Levy to be submitted to *Acta Cryst.*

(7) W. F. Zelezny and N. C. Baenziger, *J. Am. Chem. Soc.*, **74**, 6151 (1952).

The cell dimensions used in the calculation of distances,  $a = 4.315 \text{ \AA}$ ,  $c = 6.990 \text{ \AA}$ , are those of Siegel and Gebert<sup>8</sup> of Argonne National Laboratory, who kindly transmitted them to us. We are grateful to Dr. D. F. Smith of the Oak Ridge Gaseous Diffusion Plant for furnishing the compound and for valuable assistance in its manipulation.

(8) S. Siegel and E. Gebert, *J. Am. Chem. Soc.*, **85**, 240 (1963).

(9) This paper is based upon work performed at Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the Atomic Energy Commission.

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## CRYSTAL AND MOLECULAR STRUCTURE OF XENON TETRAFLUORIDE<sup>1</sup>

Sir:

Because of interest in the molecular structure of xenon tetrafluoride<sup>2</sup> we have determined the structure of the crystals by X-ray diffraction at room temperature. The structure consists of a molecular packing of square-planar molecules of XeF<sub>4</sub>.

A 4 to 1 molar ratio of F<sub>2</sub> and Xe was passed through a nickel tube at 300°. With a residence time in the hot zone of 1 minute, essentially all of the xenon reacted, and crystals condensed in the cooler part of the flow system. The solid then was sublimed under vacuum into other Pyrex containers and finally into thin-walled vitreous silica capillaries for X-ray examination.

Preliminary crystal data were obtained from oscillation and Weissenberg photographs of several crystals. The accurate cell dimensions and the intensities of the reflections were measured with a goniostat and scintillation counter with Mo K $\alpha$  radiation,  $\lambda(\text{K}\alpha_1) = 0.70926 \text{ \AA}$ . The well-formed dodecahedral crystal had diameters ranging from 0.13 to 0.24 mm., corresponding to  $\mu\text{R}$ . about unity. No correction was made for absorption. Because the crystal grew about 30% during the intensity observations, the data were normalized by repeated measurements of a few reflections.

The monoclinic unit cell has dimensions  $a = 5.050$ ,  $b = 5.922$ ,  $c = 5.771 \text{ \AA}$ . (each  $\pm 0.003 \text{ \AA}$ ),  $\beta = 99.6^\circ \pm 0.1^\circ$ , in reasonable agreement with values found elsewhere.<sup>3,4,5</sup> With 2 molecules per cell the density is 4.04 g./ml. Systematically absent reflections correspond to space group P2<sub>1</sub>/n. Reflections are strong when  $h + k + l$  is even and weak when it is odd, showing that the Xe atoms are at 0,0,0 and  $1/2, 1/2, 1/2$ . Fluorine atoms are in two sets of general positions 4(e):  $\pm(x, y, z; 1/2 - x, 1/2 + y, 1/2 - z)$ .

Intensities were measured for the 329 independent reflections of the primitive cell with  $\theta$  less than 25°. Of these, 36 are absent because of the space group symmetry. Of the other 133 reflections with  $h + k + l$  odd, whose intensities depend only on the fluorine scattering, 96 were recorded as non-zero. An extensive search for other weak reflections which would demand a larger unit cell was made by sweeping along many lattice rows and by counting at approximately 100 positions corresponding to reflections of cells with some or all of the axes doubled. No such reflections were found, with the sensitivity about 10<sup>-4</sup> of the strongest reflection.

A trial structure was derived by simple calculations involving a few reflections. It was refined by least

(1) This work was done in part under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) S. Siegel, private communication.

(4) H. A. Levy, private communication.

(5) J. A. Ibers and W. C. Hamilton, private communication.

squares in several series of calculations. With independent isotropic temperature factors and equal weights for 286 reflections (omitting the seven at the lowest angles) the conventional  $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$  was reduced to 0.086 with the parameters

	$x$	$y$	$z$	$B, \text{ \AA}^2$
Xe	(0)	(0)	(0)	1.6
F <sub>1</sub>	0.261	0.147	0.847	3.6
F <sub>2</sub>	0.228	0.033	0.295	3.7

Standard deviations are 0.003 for each coordinate. Calculations with anisotropic temperature factors gave the same coordinates within 0.002 or less. Isotropic refinement with the 96 non-zero reflections with  $h + k + l$  odd gave the same coordinates within 0.005 or less.

The above coordinates correspond to Xe-F bond distances of 1.92 and 1.90 Å., with standard deviations of 0.02 Å. The F-Xe-F bond angles are 89.7° (and 90.3°) with  $\sigma = 0.9^\circ$ . The molecule is planar by the symmetry and we find it to be square within the experimental uncertainty.

The thermal motion of the fluorine atoms exceeds that of the xenon atoms. As a result, the average Xe-F distance is greater than that given above. With the assumption that F "rides" on Xe, we estimate (from the anisotropic temperature parameters) that the average corrected distance is 1.93 Å.

The F-F distances within the molecule are 2.69 and 2.71 Å. ( $\sigma = 0.03 \text{ \AA}$ ). The shortest F-F contact between molecules is 3.02 Å.

Ibers and Hamilton<sup>5</sup> have deduced two structures by refinement of data with  $h + k + l$  even. These data do not permit determination of the relative signs of the two  $y$  coordinates. One of these two structures is in approximate agreement with our result.

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## RING CLEAVAGE OF PURINE NUCLEOSIDES TO YIELD POSSIBLE BIOGENETIC PRECURSORS OF PTERIDINES AND RIBOFLAVIN<sup>1</sup>

Sir:

The fact that adenine<sup>2,3</sup> and guanine<sup>2-4</sup> may serve as precursors of various pteridines has been amply demonstrated in several biological systems. These purines are all incorporated into the pteridine ring with resultant loss of carbon 8. Based on feeding experiments with radioactive precursors, Brenner-Holzach and Leuthardt<sup>5</sup> in studying the biosynthesis of pteridines in the *Drosophila melanogaster* have postulated that a purine nucleoside (or nucleotide) eliminates C-8 of the purine ring, and atoms 1 and 2 of ribose furnish carbons 6 and 7 of the pteridine nucleus. In the butterfly *Pieris brassicae* L. it has been shown recently by Weygand, *et al.*,<sup>6</sup> that guanoxine (or guanylic acid) serves as the direct precursor of xanthopterin and leucopterin with two of the carbon atoms of the ribosyl

(1) This work was supported by Research Grant No. T-181A from the American Chemical Society.

(2) W. S. McNutt, *J. Am. Chem. Soc.*, **82**, 217 (1960).

(3) E. Vieira and E. Shaw, *J. Biol. Chem.*, **236**, 2507 (1961).

(4) I. Ziegler-Gunder, H. Simon and A. Wacker, *Naturforsch.*, **11b**, 82 (1956).

(5) O. Brenner-Holzach and F. Leuthardt, *Helv. Chim. Acta*, **42**, 2254 (1959); **44**, 1480 (1961).

(6) F. Weygand, H. Simon, G. Dahms, M. Waldschmidt, H. J. Schliep and H. Wacker, *Angew. Chem.*, **73**, 402 (1961).