The cell dimensions used in the calculation of distances, $a = 4.315$ Å., $c = 6.990$ Å., are those of Siegel and Gebert[8] 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.

CHEMISTRY DIVISION HENRI A. LEVY
OAK RIDGE NATIONAL LABORATORY[9]
OAK RIDGE, TENNESSEE P. A. AGRON

RECEIVED DECEMBER 3, 1962

CRYSTAL AND MOLECULAR STRUCTURE OF XENON TETRAFLUORIDE[1]

Sir:

Because of interest in the molecular structure of xenon tetrafluoride[2] 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_4.

A 4 to 1 molar ratio of F_2 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 Kα radiation, $\lambda(K\alpha_1) = 0.70926$ A. The well-formed dodecahedral crystal had diameters ranging from 0.13 to 0.24 mm., corresponding to μR. 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 $a = 5.050$, $b = 5.922$, $c = 5.771$ Å. (each ± 0.003 Å.), $\beta = 99.6° \pm 0.1°$, in reasonable agreement with values found elsewhere.[3,4,5] With 2 molecules per cell the density is 4.04 g./ml. Systematically absent reflections correspond to space group $P2_1/n$. 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 θ 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^{-4} of the strongest reflection.

A trial structure was derived by simple calculations involving a few reflections. It was refined by least 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 $R = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ was reduced to 0.086 with the parameters

	x	y	z	B, Å.^{2}
Xe	(0)	(0)	(0)	1.6
F_1	0.261	0.147	0.847	3.6
F_2	0.228	0.033	0.295	3.7

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

The above coördinates 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 $\sigma = 0.9°$. 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. ($\sigma = 0.03$ Å.). The shortest F–F contact between molecules is 3.02 Å.

Ibers and Hamilton[5] 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 coördinates. One of these two structures is in approximate agreement with our result.

We thank Dr. Henri A. Levy for helpful information concerning the space group.

DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
DAVID H. TEMPLETON
ALLAN ZALKIN
J. D. FORRESTER
STANLEY M. WILLIAMSON

RECEIVED DECEMBER 15, 1962

RING CLEAVAGE OF PURINE NUCLEOSIDES TO YIELD POSSIBLE BIOGENETIC PRECURSORS OF PTERIDINES AND RIBOFLAVIN[1]

Sir:

The fact that adenine[2,3] and guanine[2-4] 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[5] 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 brassiceae L.* it has been shown recently by Weygand, *et al.*,[6] that guanosine (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).

(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).

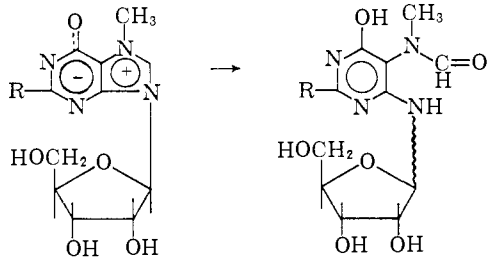
(3) S. Siegel, private communication.

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

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

group being used to complete the pyrazine ring. Stuart and Wood[7] have summarized the steps proposed for the biological transformation of guanosine to xanthopterin as follows: (a) ring cleavage of the imidazole ring of guanosine to give a 5-amino-4-ribosylaminopyrimidine. (b) Amadori rearrangement to a 1-deoxypentulose, and (c) cyclization of this ketose to a polyhydroxyalkylpteridine. These authors present support for step (b) and illustrate experimentally the ring closure of step (c). However, the most important step, (a), the controlled ring opening of the guanosine molecule, has not as yet been demonstrated either in the laboratory or in biological systems. The present communication deals with such an observed ring cleavage and thereby adds strong support to the postulations of Weygand.[6] Although 9 B-D-ribofuranosylpurine has been reported to cleave in the imidazole ring in the presence of dilute alkali[8] at room temperature, the common purine ribosides are stable under these conditions. We now have discovered that methylation at position 7 renders guanosine susceptible to ring opening in the imidazole ring under very mild conditions. 7-Methylguanosine (I)[9] is converted to the pyrimidine derivative (II) in dilute aqueous solution after several days. This reaction is considerably accelerated by the presence of aqueous ammonia. One gram of I treated with 14% aqueous ammonia and the solution left to evaporate *in vacuo* at room temperature provided, after purification, 0.6 g. of a white crystalline product which decomposed at 175–180° when placed on the melting point block at 160°; $[\alpha]^{25}D$ +32.45° (*c* 1, H_2O). The compound (II) exhibited $\lambda_{max}^{pH'}$ 270.5 mμ, ε 22,300 and $\lambda_{max}^{pH\ 11}$, 265 mμ, ε 16,300.

Anal. Calcd. for $C_{11}H_{17}N_5O_6 \cdot H_2O$: C, 39.7; H, 5.7; N, 21.0; H_2O, 5.4. Found: C, 39.8; H, 5.9; N, 21.0; H_2O, 5.1 (Karl Fischer titration).



I, R = NH_2
III, R = OH

II, R = NH_2
IV, R = OH

Such base catalyzed ring openings have been observed[10,11] for certain 7,9-disubstituted purines. The opening of the imidazole ring probably is due to the attack of hydroxyl ion at the electrondeficient 8-position.

Methionine has been shown to be the primary precursor of the methyl groups[12–14] of N-methyl-purines, such as 7-methylguanine, which have been isolated from various biological sources. Inspection of formulas I and II strongly suggests the possibility that such derivatives might well be biogenetic precursors of N^5-methyltetrahydrofolic acid,[15,16] a functional form of folic acid. The N^7-methyl group required for the ring opening of guanosine presumably could become the N^5-methyl group of N^5-methyltetrahydrofolic acid (prefolic A). This possibility receives support from the work of Reynolds and Brown[17] who have shown that cell-free extracts of *E. coli* can convert guanosine to derivatives of folic acid.

7-Methylxanthosine (III)[9] similarly opens in the imidazole ring to provide IV as a crystalline solid in 60% yield, dec. 155–160°; $[\alpha]^{25}D$ +20.8° (*c* 1, H_2O); $\lambda_{max}^{pH\ 1}$, 268 mμ ε 20,700; $\lambda_{max}^{pH\ 11}$, 269 mμ, ε 15,000.

N.m.r. spectra[18] of I and III showed a very sharp singlet at 9.6 and 9.4 δ, respectively, due to the C^8 proton of the imidazole ring. N.m.r. of compounds II and IV showed the absence of this band, which was replaced by a new broader absorption band at 8.15 δ characteristic of the C proton of a formylamino group. II and IV exhibited a single spot (absence of starting material) when chromatogrammed in three solvent systems. Acid hydrolysis of II and IV provided D-ribose as one of the products, which was identified by means of paper chromatography.[19] Although the β-configuration and the furanose ring might be inferred in compounds II and IV, the precise structure and configuration of the ribose moiety is presently under investigation.

Neilson and Wood[20] have pointed out that on the basis of present evidence a purine nucleoside is the most likely biogenetic precursor of riboflavin and that cleavage of the imidazole ring to give a compound such as 5-amino-4-ribosylaminouracil probably is the first step in such a transformation. It is of considerable interest that IV bears such close structural relationship to this postulated precursor of riboflavin.

These observations await exploration in biological systems.

(7) A. Stuart and H. C. S. Wood, *Proc. Chem. Soc.*, 151 (1962).
(8) M. P. Gordon, V. S. Weliky and G. B. Brown, *J. Am. Chem. Soc.*, **79**, 3245 (1957).
(9) J. W. Jones and R. K. Robins, *ibid.*, **85**, 193 (1963).
(10) P. Brookes and P. D. Lawley, *J. Chem. Soc.*, 3923 (1961).
(11) H. Bredereck, G. Kupsch and H. Wieland, *Ber.*, **92**, 583 (1959).
(12) L. R. Mandel and E. Borek, *Biochem. Biophys. Research Comm.*, **4**, 14 (1961).
(13) L. Anderson and M. Gibbs, *J. Biol. Chem.*, **237**, 1941 (1962).
(14) B. B. Biswas, M. Edmonds and R. Abrams, *Biochem. Biophys. Research Comm.*, **6**, 146 (1961).
(15) A. R. Larrabee, S. Rosenthal, R. E. Cathou and J. M. Buchanan, *J. Am. Chem. Soc.*, **83**, 4095 (1961).
(16) K. O. Donaldson and J. C. Keresztesy, *J. Biol. Chem.*, **237**, 1298 (1962).
(17) J. J. Reynolds and G. M. Brown, *ibid.*, **237**, PC2713 (1962).
(18) Observed in dimethylsulfoxide with tetramethylsilane as an external standard.
(19) S. M. Partridge, *Nature*, **158**, 270 (1946).
(20) T. Neilson and H. C. S. Wood, *J. Chem. Soc.*, 44 (1962).

DEPARTMENT OF CHEMISTRY LEROY B. TOWNSEND
ARIZONA STATE UNIVERSITY
TEMPLE, ARIZONA ROLAND K. ROBINS

RECEIVED AUGUST 16, 1962

TETRAKIS-(DIMETHYLAMINO)-ETHYLENE. II.[1] THE REACTION WITH BORON TRIFLUORIDE

Sir:

Carbenes CX_2 with electron donating substituents X (NR_2, OR, F) should be more stable than methylene CH_2.[2] Therefore we considered the possibility of an equilibrium [Ethylene ⇄ 2 Carbene] in the case of tetrakis-(dimethylamino)-ethylene (I)

$$\underset{\text{I}}{(MeN)_2C{=}C(NMe_2)_2} \rightleftarrows \underset{\text{II}}{2(Me_2N)_2\bar{C}} \qquad \underset{\text{III}}{(Me_2N)_2\overset{\oplus}{C} \rightarrow \overset{\oplus}{B}\mp_3}$$

In order to prove the existence of bis-(dimethylamino)-carbene (II) we wanted to trap II in the form of its BF_3 adduct, bis-(dimethylamino)-carbene–boron trifluoride (III).

Boron trifluoride-diethyl-ether was added dropwise to an ethereal solution of I at −20°. A colorless solid formed with evolution of heat. It consisted of a little octamethyloxamidinium-tetrafluoroborate[1] (IV, mechanism of formation unknown) and a large amount of tetrakis-(dimethylamino)-ethylene-difluoroboron-tetrafluoroborate (V) (colorless needles from methanol, m.p. 217° dec., stable to air and water).

(1) Part I: Nils Wiberg and J. W. Buchler, *Angew. Chem.*, **74**, 490 (1962).
(2) H.-W. Wanzlick, *ibid.*, **74**, 129 (1962).