

TABLE I
ULTRAVIOLET ABSORPTION DATA

| DL-Chromenol | | E_1 $^{1\%}$ cm at λ_{max} . μ | | |
|--------------|-----|--|-----|-----|
| | | 232 | 274 | 280 |
| V | 233 | 97 | 92 | 40 |
| VI | 310 | 126 | 119 | 50 |
| VII | 598 | 254 | 215 | 101 |
| VIII | 382 | 159 | 150 | 65 |

The activated hydrogen of quinone A is removed as a proton by the hydride ion forming an anion and hydrogen. The anion is considered a resonance hybrid of the resonance structures carbanion B and alkoxide ion C. The alkoxide ion has an electronic configuration suitable for cyclization. Electron shift, initiated by polarization of the carbonyl group, causes cyclization to an aromatic system and gives the phenolate ion D.

The better yields obtained by use of sodium hydride may be due to the "irreversibility" of the first step, and the selectivity of this reagent. Not all of the quinone is converted to the chromenol; apparently part is reduced by the hydride. The resulting hydroquinone is air-oxidized to the quinone during purification. The selectivity of this reagent appears to be unique, and can be appreciated when considering the high reactivity of the methoxy groups. For example, such groups are rapidly replaced by bases, such as the alkoxides^{12,13} and amines.

(12) B. O. Linn, N. R. Trenner, B. H. Arison, R. G. Weston, C. H. Shunk and K. Folkers, *J. Am. Chem. Soc.*, **82**, 1647 (1960).

(13) C. H. Shunk, D. E. Wolf, J. F. McPherson, B. O. Linn and K. Folkers, *ibid.*, **82**, 5914 (1960).

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CRYSTALLOGRAPHIC STUDIES OF XeF₂ AND XeF₄¹

Sir:

The preparation of XeF₄ has been described by Claassen, Selig and Malm.² In this study, the existence of a lower fluoride was suggested, and a difluoride, XeF₂, was subsequently prepared by Smith.³ We wish to report on the structure of XeF₂ prepared by a photochemical process⁴ and to present crystallographic data for XeF₄.

XeF₂ is tetragonal with $a = 4.315 \pm 0.003$ Å. and $c = 6.990 \pm 0.004$ Å. Space group I4/mmm has been assigned with xenon atoms in 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. This leads to a density value of 4.32 g./cm³. for two molecules in the cell. Single crystal and powder data recorded photographically indicate that the four fluorine atoms are probably in positions 00z, 00 \bar{z} , + *b.c.* The very high absorption for the CuK α radiation used in this study and the weak fluorine contributions do not permit an accurate determination of *z*. However, a value $z = 0.306 \pm 0.020$ produces a noticeable improvement in agreement between calculated and observed intensities. This leads to linear F-Xe-F molecules with Xe-F distances of 2.14 ± 0.14 Å.

Crystals condensed from XeF₄ vapor at room temperature have been found to exhibit more than one symmetry. A monoclinic form frequently observed

(1) Based on work performed 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) D. F. Smith, *J. Chem. Phys.*, in press.

(4) J. L. Weeks, C. L. Cherrick and M. S. Matheson, *J. Am. Chem. Soc.*, **84**, 4612 (1962).

has dimensions $a = 5.03$ Å., $b = 5.92$ Å., $c = 5.79$ Å., and $\beta = 99^\circ 27'$. The extinctions, based on single crystal observations with X-rays, correspond to space group P2₁/n. One can account for the intensities generally by placing xenon atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Thus, with 2 molecules in the cell, the X-ray density is 4.04 g./cm³. Attempts to locate fluorine positions by X-rays have been unsuccessful because of the very high absorption errors. The assigned space group will permit a planar configuration. However, only a few weak fluorine dependent reflections have been found and one must therefore allow for the possible selection of a different space group. Neutron diffraction data probably will be required in order to locate fluorine positions.

Another form has been found, apparently monoclinic, but distinct from the above modification.

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MOLECULAR SYMMETRY OF XeF₂ AND XeF₄

Sir:

The recent preparation¹ of XeF₂ and XeF₄ has led us to consider the molecular structures of these compounds in terms of a programmed² semiempirical LCAO molecular orbital theory. A linear structure for XeF₂ and a square-planar structure for XeF₄ are indicated, as would be expected by analogy to^{3,4} ICl₂⁻¹ and ICl₄⁻¹. (IF₄⁻¹, isoelectronic with XeF₄, is known,⁵ but its structure is not.)

The basis set consisted of four Slater orbitals of s and p types from each fluorine and nine orbitals of s, p, and d types from xenon. Orbital exponents are $c_s = 2.97$, $c_p = 2.30$, $c_d = 3.71$ for Xe, and $c_s = c_p = 2.42$ for F. Coulomb integrals in e.v. are $Q_s = -30$, $Q_p = -15$, $Q_d = -25$ for Xe, and $Q_s = -31.4$ and $Q_p = -17.4$ for F. The elements of the effective one-electron Hamiltonian matrix H are related to the overlap matrix S by

$$H_{ij} = -2(H_{ii} \cdot H_{jj})^{1/2} S_{ij}, \quad i \neq j \quad (1)$$

where H_{ii} is the coulomb integral associated with the *i*th atomic orbital. The eigenvalues λ_j obtained from the solution of

$$Hc = \lambda Sc \quad (2)$$

are used in defining the total orbital energy *E* as

$$E = \sum_j n_j \lambda_j \quad (3)$$

where n_j is the occupation number (0, 1 or 2) of the *j*th MO. The bond energy for XeF_{*n*} is defined as

$$BE = (1/n) \left(\sum_j m_j H_{ii} - E \right) \quad (4)$$

where the energy of the atoms at infinite separation is taken to be $\sum_j m_j H_{ii}$, with *m* being the occupation number of the *i*th AO in the ground state of the free atom.

The results are shown in Table I. Assumption of either smaller xenon exponents or larger (in magnitude) xenon coulomb integrals gave less favorable bonding energies. We consider 16 electron pairs and 17 MO's for XeF₂, while there are 23 electron pairs and 25 MO's for XeF₄. For Xe-F distances taken greater

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

(2) T. Jordan, H. W. Smith, L. L. Lohr, Jr. and W. N. Lipscomb, to be published.

(3) R. C. L. Mooney, *Z. Krist.*, **100**, 519 (1939).

(4) R. C. L. Mooney, *ibid.*, **98**, 377 (1938).

(5) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 2373 (1960).

TABLE I
THEORETICAL RESULTS

| Symmetry | Xe ⁻ F | -E, e.v. | BE, e.v. | λ, e.v., of highest MO's Occupied | | | |
|------------------------------------|------------------------------|-------------|-------------|--------------------------------------|-------|-------|-------|
| XeF ₂ : D _{∞h} | 2.4 | 707.0 | 3.3 | -11.3 | -14.9 | -14.9 | |
| | C _{2v} ^a | 2.4 | 705.5 | 2.6 | -12.1 | -13.8 | |
| | C _{4v} ^a | 2.4 | 704.0 | 1.8 | -12.8 | -13.0 | |
| XeF ₄ : D _{4h} | 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 _{4v} ^b | 2.4 | 1007.7 | 1.9 | -12.1 | -12.3 | -12.3 |
| | C _{2v} ^b | 2.4 | 1009.6 | 2.4 | -11.2 | -12.8 | -12.8 |
| | T _d | 2.4 | 1007.4 | 1.8 | -12.3 | -12.3 | -12.3 |

^a Assumed bond angle of 120° for C_{2v} and 90° for C_{2v}'.

^b Assumed bond angles of 70° 32' for C_{4v} and 90° for C_{2v}.

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_{4h}, $a_1 + e$ in C_{4v}, $a_1 + b_2$ in C_{2v}, t_2 in T_d, and $\sigma_u + \pi_u$ in D_{∞h}. As the two highest MO's are vacant in XeF₄, T_d symmetry does not correspond to a closed shell configuration. Now, as $\lambda_e < \lambda_a$ in C_{4v}, but $\lambda_{a_{2u}} < \lambda_{e_u}$ in D_{4h}, the latter symmetry corresponds to a closed-shell, while the former does not. For XeF₂ 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 XeF₂ with D_{∞h} symmetry arises primarily from the relatively lower energy of the two occupied, antibonding π_u MO's consisting largely of xenon 5p orbitals perpendicular to the bond axis. Similarly, a D_{4h} symmetry is favored for XeF₄ 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 XeF₄ (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_{4v} model of IF₅, 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 XeF₄ from an overestimation of interactions involving the xenon 5s orbital (or possibly 5p orbitals). The results obtained for XeF₅ 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.²

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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 xenon¹ are of interest in clarifying the nature of their chemical binding, a neutron diffraction study of XeF₂ at room temperature has been undertaken. A sample furnished by D. F. Smith, who recently reported²

(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 diffractometer³ 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,⁴ yielded the over-all scale factor and these parameters, listed with their standard errors appended in parentheses

| | δ | β_{11} | β_{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 foreshortened⁵; a corrected mean separation,⁶ 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 XeF₂ 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. found⁷ in the pseudo-isoelectronic ion ICl₂⁻, if correction is made for the difference in radius of Cl and F, and qualitative allowance is made for the negative ionic charge. However, Smith² 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).