

TABLE I
ULTRAVIOLET ABSORPTION DATA

DL-Chromenol		$E_1^{1\% \text{ cm at } \lambda_{\text{max.}}}$ μ		
		274	280	330
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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RECEIVED NOVEMBER 13, 1962

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 $a = 4.315 \pm 0.003 \text{ \AA}$. and $c = 6.990 \pm 0.004 \text{ \AA}$. 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} , $\pm b.c.$ 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 $2.14 \pm 0.14 \text{ \AA}$.

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. Malin, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

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

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

has dimensions $a = 5.03 \text{ \AA}$., $b = 5.92 \text{ \AA}$., $c = 5.79 \text{ \AA}$., 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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RECEIVED NOVEMBER 19, 1962

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. Malin, *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).