Fig. 2. *Bis-o*-phenylene*bis*(dimethylarsine)carbon(IV) tetraperchlorate

is simply a gradual transition from Li(I) to C(IV) as the formal charge on the central atom increases.

The X-ray diffraction powder pattern of *bis-o*-phenylene-*bis*(dimethylarsine)carbon(IV) tetrabromide shows that the salt is not isomorphous with the corresponding Ti(IV) complex, $TiCl_4.2$ diarsine; a full structural determination by Dr. P. Pauling is in progress.

The extension of these investigations to GeI_4 and the other group IV halides and to the trihalides of group V elements is in progress. Previous work by Sutton[5] led to the isolation of derivatives of the type PCl_3 diarsine in which the five-co-ordinate phosphorus atom is almost certainly square pyramidal owing to the presence of a lone pair of electrons. There is evidence that by using more vigorous conditions removal of halogen atoms from the co-ordination sphere can be effected.

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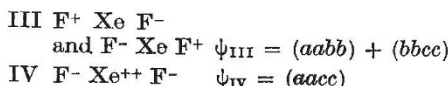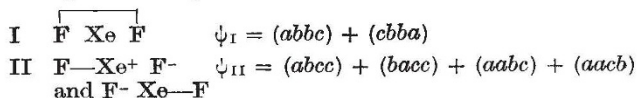R. S. Nyholm
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Electronic Structure of Xenon Difluoride

This communication describes the results of some very approximate calculations relating to the electronic structure of XeF_2. The treatment is of the four electrons associated with a framework: $F^+Xe^{++}F^+$. The various wave functions of the molecule which were tested were constructed from the $2p_z$ orbitals of the two fluorine atoms and the $5p_z$ orbital on the xenon atom, the three atoms being in a straight line along the z-axis. It has been assumed that, for this approximate treatment, other atomic orbitals can be neglected. The excitation of an electron from a $5p$ to a $6s$ orbital in a xenon atom requires about 8·25 eV and to a $5d$ orbital about 10 eV, and from a $2p$ to a $3s$ orbital in a fluorine atom about 12 eV[1]. These are such large energies that the restriction to the p-orbitals seems to be reasonable.

There are four independent configurations of the correct symmetry which can be constructed using the three p-orbitals. Using a valence bond formulation these may be represented by:

I   F̄ Xe F̄ $\psi_I = (abbc) + (cbba)$

II F—Xe⁺ F⁻ $\psi_{II} = (abcc) + (bacc) + (aabc) + (aacb)$
    and F⁻ Xe—F

III F⁺ Xe F⁻
    and F⁻ Xe F⁺ $\psi_{III} = (aabb) + (bbcc)$

IV F⁻ Xe⁺⁺ F⁻ $\psi_{IV} = (aacc)$

where a, b and c represent the p-orbitals on the three atoms F, Xe and F. The symbol $abbc$ symbolizes the anti-symmetrized determinant with the spin-functions assigned in the order $\alpha\beta\alpha\beta$.

The following gives a summary of the way in which the values for the integrals for the configuration interaction and approximate treatments were obtained. The overlap integral $\int ab$ was calculated using $Z'(F) = 2·6$ and $Z'(Xe) = 2·15$[2] and a XeF distance of 2·0 Å (ref. 3); $\int ac$ was taken to be zero. The kinetic energy integrals $\int a|\Delta|a$ and $\int b|\Delta|b$ were given values obtained from ionization potential data, using the Virial Theorem; $\int a|\Delta|b$, etc., were calculated using Roothaan's formula with Slater orbitals[4]. The core integrals $\int a : aa$ and $\int b : bb$ were given values obtained from ionization potential data. Assuming that both the electron charge distributions, aa and bb, could be approximated using two given spherical charge distributions (since both a and b are p orbitals) an effective nuclear charge was chosen for each centre and, using these, $\int a : bb$, $\int a : ab$, etc., were calculated. The electron–electron repulsion integrals were also calculated using these spherical charge distributions. The value for $\int aa : aa$ agreed approximately with the value expected from the difference between the ionization potential and electron affinity of the fluorine atom and that for $\int bb : bb$ with the difference between the appropriate first and second ionization potentials of the xenon atom. It is true that the exact values of these integrals must be unreliable, but their relative magnitudes and their general pattern is almost certainly correct. Consequently they are most likely to be adequate to decide which approximate wave function gives the lowest energy and, therefore, the most satisfactory simple representation of the electronic structure. The configuration interaction treatment gives an energy of $-161·73$ eV with the function $0·223 \psi_I + 0·270 \psi_{II} + 0·039 \psi_{III} + 0·547 \psi_{IV}$. The results for various

Table 1. Results using Various Approximate Functions

Type	Wave function	Constant	Energy (eV) E	$E—E_{CI}$
Molecular orbital	$(a+kb+c)^2 (a-c)^2$	$k=1$	$-161·07$	$0·66$
		$k=\sqrt{2}$	$-160·04$	$1·69$
		$k=0·78$ (best)	$-161·26$	$0·47$
Heitler, London	ψ_{II}	—	$-158·14$	$3·59$
Bond orbitals	$(a+kb)^2c^2 + a^2(c+kb)^2$	$k=1$	$-157·90$	$3·83$
		$k=0·51$ (best)	$-160·43$	$1·30$
Coulson Fischer	$(a+kb)(b+ka)cc + (c+kb)(b+kc)aa +$ equivalent terms	$k=4·62$ (best)	$-159·45$	$2·28$
NPSO (ref. 5) (non-paired spatial-orbitals)	$a(a+kb)(kb+c)c +$ equivalent terms	$k=1$	$-161·61$	$0·12$
		$k+0·92$ (best)	$-161·65$	$0·10$
Configuration interaction	See text	—	$-161·73$	0

approximate wave functions are shown in Table 1 (compare with Hirst and Linnett[5]); in each case a calculation has been made in which the energy has been minimized with respect to a variable k. The result indicates that the wave function based on the formula

$$\overset{\cdot|}{—F} \cdot \overset{|}{Xe} \cdot \overset{|\cdot}{F—}$$
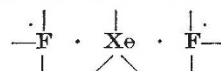
is the best of those tested. Moreover, the calculated energy for this function is very close to that obtained using the full configuration interaction treatment.

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