

### 892. *The Electronic Structure of Dioxygen Difluoride.*

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An explanation of the short O-O bond and the long O-F bonds in dioxygen difluoride is suggested.

It has been shown recently that dioxygen difluoride is FOOF.<sup>1</sup> The O-F bond length (1.58 Å) is much greater than that in OF<sub>2</sub> (1.41 Å),<sup>2</sup> and the O-O bond length (1.22 Å) is essentially the same as that in O<sub>2</sub> (1.21 Å),<sup>3</sup> being much shorter than that in H<sub>2</sub>O<sub>2</sub> (1.48 Å),<sup>4</sup> and even than that in O<sub>2</sub><sup>-</sup> (1.28 Å).<sup>5</sup> The F-O-O angle is 109½° and the dihedral angle 87½°. The barrier is high.

<sup>1</sup> Jackson, *J.*, 1962, 4585.

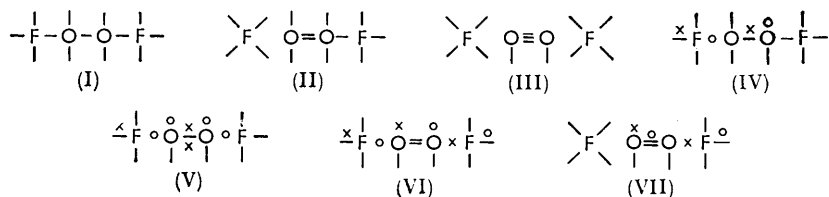
<sup>2</sup> Pierce, Jackson, and DiCianni, *J. Chem. Phys.*, 1961, **35**, 2240.

<sup>3</sup> Babcock and Herzberg, *Astrophys. J.*, 1948, **180**, 167.

<sup>4</sup> Abrahams, Collin, and Lipscomb, *Acta Cryst.*, 1951, **4**, 15.

<sup>5</sup> Abrahams and Kalnajs, *Acta Cryst.*, 1954, **7**, 838.

If the double-quartet modification of the octet rule is used,<sup>6</sup> ten structures are possible for this molecule. They are (I)—(VII) and the "mirror images" of (II), (IV), and (VII). In the Table are listed the formal charges on the atoms for each structure,



together with the number of electron-pairs which are occupying the same bond or lone-pair orbital. The number of close spatial pairs can be deduced by supposing that, round every atom, the four electrons of a given spin have a tetrahedral arrangement. If it is supposed that the structures that will be the most important are those that (a) have small formal charges on the atom, and (b) reduce interelectron repulsion because the electrons

Formal charges on the atoms F, O, O, and F in  $O_2F_2$  for the structures (I)—(VII), together with the number of electron-pairs occupying the same bond or lone orbitals.

Structure	Formal charges on				Number of close pairs	Structure	Formal charges on				Number of close pairs
	F	O	O	F			F	O	O	F	
(I)	0	0	0	0	7	(V)	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	0
(II)	-1	0	+1	0	6	(VI)	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	0?
(III)	-1	+1	+1	-1	2?	(VII)	-1	$+\frac{1}{2}$	+1	$-\frac{1}{2}$	0
(IV)	$-\frac{1}{2}$	0	$+\frac{1}{2}$	0	1						

of one spin possess a different spatial pattern from those of the other, then the four most important structures will be (IV) and its mirror image, (V), and (VI). Structure (VI) will separate the electrons of one spin from those of the other if the two electrons of one spin in the O—O bond have a high probability of being in a plane at right angles to the two of the other spin. With this arrangement, the FOO planes would be at right angles to one another. For the other three structures, there is no such strongly directing effect on the mutual orientation of these two planes. However, if (VI) is an important contributor, the two planes would be expected to be at right angles. The experimental value for the angle between them is  $87\frac{1}{2}^\circ$ .

The formal charges of  $+\frac{1}{2}$  and  $-\frac{1}{2}$  on oxygen and fluoride would seem to be allowable energetically since  $H_3O^+$  and  $F^-$  are stable under ordinary conditions. Structure (IV) and its "mirror image" appear to be preferred since they involve only two formal charges of  $|\frac{1}{2}|$  whereas (V) and (VI) involve four. On the other hand, each of these structures places one pair of electrons in the same bond orbital and so interelectron repulsion will be greater for them than for (V) and (VI). *A priori*, one would be tempted to suggest that all these four structures would be important and that the O—O bond length would be about 1.24 Å, roughly mid-way between that in  $O_2^-$  (XI)<sup>6</sup> and  $O_2$  itself, with the shorter bond favoured slightly (cf. C—C in benzene). In fact, the O—O and F—O bond lengths seem to suggest that (V) and (VI) are more important than (IV) and its mirror image. Moreover, the importance of (VI) will account for the high resistance to the twisting of the two OOF planes away from an interplane angle of  $90^\circ$ , since this would bring the two electrons of one spin in the O—O bond close to the other two in this structure. The F—O—O angle might have been expected to be a little larger than it is but, on the other hand, bond angles involving bonds to fluorine are always smaller than corresponding angles involving other atoms (cf.  $OH_2$  and  $OF_2$ ). The observed shape of FOOF can therefore be understood by using the double-quartet formulation of the octet together with

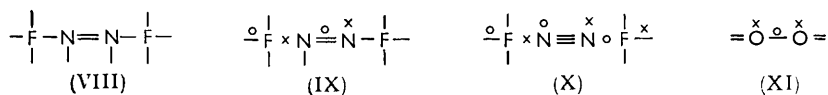
<sup>6</sup> Linnett, *J. Amer. Chem. Soc.*, 1961, **83**, 2643.

the following guiding principles for choosing which structures will correspond to electron distributions having the lowest energy and therefore the greatest importance: (1) disposal of the electrons of one spin in a different spatial pattern from those of the other will lower the interelectron repulsion energy; (2) the existence of formal charges on atoms will lead to an increase in energy but a guide to the magnitude of this can be obtained by considering the stability of simpler systems (*e.g.*,  $\text{OH}_3^+$ ,  $\text{OH}^-$ ,  $\text{NH}_4^+$ , and  $\text{F}^-$  are stable but not  $\text{H}_2\text{F}^+$ ); it is supposed that this makes it possible to decide whether a given formal charge is allowable energetically or not.

The interpretation suggested by Lipscomb (see ref. 1) corresponds in some respects to the present one; it employs a different basis for the description and does not lead easily to specific conclusions regarding what dimensions and shape are to be expected. The ordinary valence-bond description differs from the present one because it employs only structures (I), (II) and its mirror image, and perhaps (III).

The reason why  $\text{HOOH}$  has a structure similar to (I) is that all others are unimportant because they place a negative formal charge on at least one H atom and this represents an electron concentration of too high energy. (No stable compound is known for which there is any evidence that structures which give a formal negative charge to a hydrogen atom are important.)

The arguments used in this paper will lead to the expectation that the structures that must be considered for  $\text{FNNF}$  are (VIII), (IX) and its mirror image, and (X). Of these, (VIII) gives zero formal charges on every atom but requires that six pairs of electrons occupy the same bond or lone-pair orbitals. Structure (IX) and its "mirror image" separate electrons of different spin and the formal charges ( $-\frac{1}{2}$ , 0,  $+\frac{1}{2}$ , 0) are reasonable. On the other hand, the electrons of one spin favour one  $\text{NNF}$  grouping's being linear while the other favours its being bent. Structure (X) favours a linear arrangement for the whole



molecule and the pattern of tetrahedra is not such that the electrons of different spin can be kept apart. A structure for  $\text{N}_2\text{F}_2$  analogous to (V) for  $\text{O}_2\text{F}_2$  is impossible. Consequently, it seems probable that the important structures will be (VIII) and (IX) and its mirror image. The molecule would therefore be expected to be planar, which it is. The N-F bond would be expected to be longer than in  $\text{NF}_3$  but the percentage difference would be expected to be less than between  $\text{O}_2\text{F}_2$  and  $\text{OF}_2$ . The values are:  $\text{N}_2\text{F}_2$ ,  $1.44 \pm 0.04$ ;  $\text{NF}_3$ ,  $1.371$ .<sup>8</sup> The percentage difference for the nitrogen compound is 5% and for the oxygen compounds 12%. The N-N bond would be expected to be a little shorter in  $\text{N}_2\text{F}_2$  than in  $(\text{CH}_3)_2\text{N}_2$ . The experimental figures are  $1.25 \pm 0.02$  and  $1.24 \pm 0.05$ .<sup>9</sup> The data are not, therefore, sufficiently accurate to answer the last question though they do suggest that the reduction (if any) is not as great as would have been expected.

The data for the molecules  $\text{S}_2\text{Cl}_2$  and  $\text{S}_2\text{Br}_2$ , which seem to fall into the same pattern,<sup>1</sup> will not be discussed here because it is difficult to know whether the number of electrons associated with the sulphur atoms should be restricted to eight in these molecules.

<sup>7</sup> Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104.<sup>8</sup> Sheridan and Gordy, *Phys. Rev.*, 1950, **79**, 513.<sup>9</sup> Boersch, *Sitzungsber. Akad. Wiss. Wien*, 1935, **144**, 1.