The Effective Shape of the Covalently Bound Fluorine Atom

By S. C. NYBURG and J. T. SZYMAŃSKI

(*Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada*)

IT has been generally accepted[1] that the van der Waals radius of covalently bound fluorine is about 1·35 Å, although 1·49 Å has been cited.[2] The smallest value appears to be that of 1·33 Å in ClF_3.[3] If the effective shape of the bound fluorine atom is spherical and the radius 1·33 Å, one can make a fairly accurate prediction of the density of solid molecular fluorine, assuming hard spheres and an F–F bond length of 1·42 Å. It is known that there are some three space groups likely for packing diatomic homopolar molecules, in the hexagonal, cubic, and orthorhombic[4] systems, or space groups closely related to these by minor molecular shifts. The calculated densities for solid F_2 on this basis would be about 2·8 g. c.c.$^{-1}$, whereas it has been shown[5] that the density of the lowest polymorph, α-F_2, is 1·78 g. c.c.$^{-1}$ at 45·6° K and 1·90 at 20° K.

The structure analysis of α-F_2 at 20° K has recently been undertaken by Meyer and Barrett.[6] The structure appears to be isomorphous with that of α-O_2 [7] and resembles a nearly-hexagonal array of molecules not quite perpendicular to the basal plane. The structure, which is partially disordered, and has a calculated density of 1·96 g.c.c.$^{-1}$, is a closed one and the thermal parameters are small. Therefore the effective radius of the covalently bound fluorine atoms must be substantially greater than 1·33 Å, at least in certain directions α

TABLE

	Observed X–F · · · F (deg.)	r derived from curve (Å)	$r_1 + r_2$ from curve (Å)	F · · · · F observed (Å)	Ref.
BrF_5	179·5	1·34	2·68	2·71	9
	175·7	1·34			
ClF_3	170·0	1·34	2·68	2·66	3
	170·0	1·34			
IF_7	164·3	1·35	2·70	2·70	9
	167·5	1·35			
BrF_3	143·5	1·34	2·73	2·72	9
	175·6	1·39			
IF_7	141·9	1·48	2·88	2·88	9
	118·4	1·40			
BrF_5	115·9	1·49	2·98	3·00	9
	116·9	1·49			
BrF_3	91·8	1·50	3·04	3·01	9
	117·4	1·54			

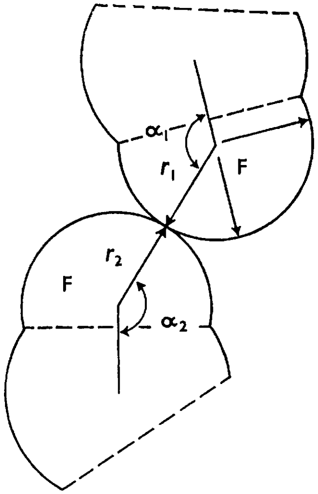

FIGURE 1. *Angles α_1, α_2 and distances r_1, r_2 for two F atoms in contact.*

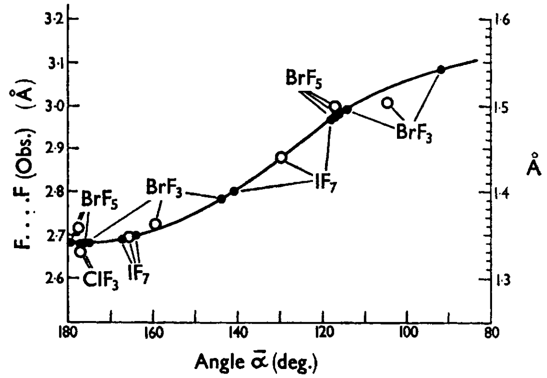

FIGURE 2. ○, *observed* F · · · · F *distances* (*left hand ordinate*) versus $\bar{\alpha}$; ●, *derived values of* r_1 *and* r_2 (*right hand ordinate*) versus *observed* α_1 *and* α_2.

(Figure 1), with respect to the internuclear axis. We examined a large number of published crystal structures containing covalently bound fluorine and plotted nearest unbound F · · · · F distances between different molecules against the mean value of α_1 and α_2 (Figure 2).

The values plotted were the smallest found at any given $\bar{\alpha}$. There are many instances of *larger* F · · · · F values at a given $\bar{\alpha}$ which may arise because other-atom conflicts are preventing close F · · · · F contact or because of high thermal parameters. We observed smaller F · · · · F contacts in only one crystal structure, that of C_8F_{12}.[8] This structure is disordered so that these short, statistically-averaged distances can be explained on other grounds.

The curve obtained by plotting $\bar{\alpha}$ against F · · · · F values can be used for obtaining approximate r_1 and r_2 values at α_1 and α_2. From these values the curve can be slightly modified as necessary, to give the self-consistent set of r_1 and r_2 values given in the Table. It is clear that the effective radius of fluorine is about 1·34 Å for end-on contact but is significantly greater as α decreases from 180°. It is not feasible to extend the curve much below 90° since the atom to which fluorine is bonded begins to interfere at this acute angle. Thus the observed F · · · · F of 3·00 Å in SiF_4 has simply been halved in ref. 2. However α_1 and α_2 are 80·4 and 150·9°. If we take r_2 as 1·375 Å from the curve in Figure 1 then r_1 will be 1·625 Å which lies above the curve, as might be expected.

If the atoms in the F_2 molecule are represented by oblate semi-spheroids with major radii 1·34 and 1·55 Å (Figure 1) and the molecules close-packed in hexagonal $P\bar{6}m2$, the density is 2·12 g. c.c.$^{-1}$ which, when one considers the extreme close packing in this hypothetical structure, is in good agreement with the observed 1·96 g. c.c.$^{-1}$ for the presumably slightly less close-packed α-F_2.

The cause of the effectively non-spherical shape of bound fluorine may lie in the molecular multipole interactions. This aspect of the problem is currently under study.

(*Received, March 4th,* 1968; *Com.* 269.)

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