

THE ESR STUDY OF THE BF_2 RADICAL PRODUCED IN THE γ -IRRADIATED SINGLE CRYSTAL OF BF_3

Kunihisa SOGABE*

Abstract: ESR spectra of the radicals produced in polycrystal and single crystal of BF_3 under γ -irradiation at 77 K were investigated. From analyses of these spectra, the radicals were identified as BF_3^- and BF_2 radicals, respectively. ESR parameters of these radicals were the very same with those reported in literatures.^{1,2)} Furthermore, the analyses showed that an interesting long-range interaction of the BF_2 radical with the nearest neighboring two molecules is involved and the distance between the BF_2 radical and the nearest neighboring fluorine atom is *ca.* 2.8 Å.

INTRODUCTION

ESR studies of a fluorine-containing radical were of considerable undertaken because a fluorine nucleus exhibits a large hyperfine splitting and formations of radicals are affected by various environments.^{2,3)} Phosphoranyl radicals of $\text{PF}_n\text{H}_{4-n}$ type³⁾ were prepared by γ -irradiations of various matrices containing PF_3 , PF_2H , and PH_3 , respectively. Nelson and Gordy²⁾ reported an ESR spectrum of a BF_2 radical created by a γ -irradiation of a BF_3 molecule in xenon matrix at 4.2 K and no spectrum of a BF_2 radical in krypton matrix. Furthermore, they deduced a bond angle of the BF_2 radical to be 112° from an analysis of an isotropic hyperfine splitting.

A structure of the BF_2 radical was long-established by a UV emission spectrum⁴⁾ and a MO calculation using a INDO method.⁵⁾ Zaucer and Azman⁶⁾ speculated spin densities on the BF_2 radical reported by Nelson and Gordy and obtained the values fairly agreed with that estimated from the ESR result. Many SCFMO calculations⁷⁾ on the bond angle of the BF_2 radical were reported so far, but all values were significantly larger than that deduced from the ESR parameters. Accordingly, the structure of the BF_2 radical is rather less certain and further studies on the BF_2 radical would be desirable.

As a rule, such a study on a single crystal facilitates the accurate interpretation of the

experimental data substantially and also makes possible the direct comparison with the results on the polycrystal. However, a single crystal of such a molecule as BF_3 with low boiling point was very difficult to prepare and was still not reported even X-rays studies until today. In more recently, Hasegawa *et al.*⁸⁾ successfully prepared single crystals of PF_3 and SiF_4 at 77 K and determined the structures of the PF_4 and SiF_3 radicals produced in γ -irradiated single crystals of PF_3 and SiF_4 , respectively. Subsequently, present author intended to prepare the single crystal of BF_3 and to investigate the formations and the structures of the radicals produced in the γ -irradiated single crystal of BF_3 .

EXPERIMENTAL

Boron trifluoride, BF_3 , was purchased from Hashimoto Chemicals and stated having its minimum purity of 99.7% by supplier. Gas was further purified by three vacuum distillations before use and introduced into an ESR sample tube through a grease-cut trap or greaseless cock. Single crystals were prepared as follow: crystal growth was successful by controlling a steep temperature gradient in liquid nitrogen from neary its melting point (-127°C). All samples were subjected to γ -irradiations at 77 K by ^{60}Co source with effective dosages of *ca.* 1 M rad/h for 30-35 hr.

ESR spectra were recorded at 77 K without permitting the temperature to rise during handling. The reproducibility of ESR data from one sample to another served as an excellent check on the single crystallinity of a particu-

* Department of Chemistry, Faculty of Education, University of Shimane, Matsue, Japan. 690

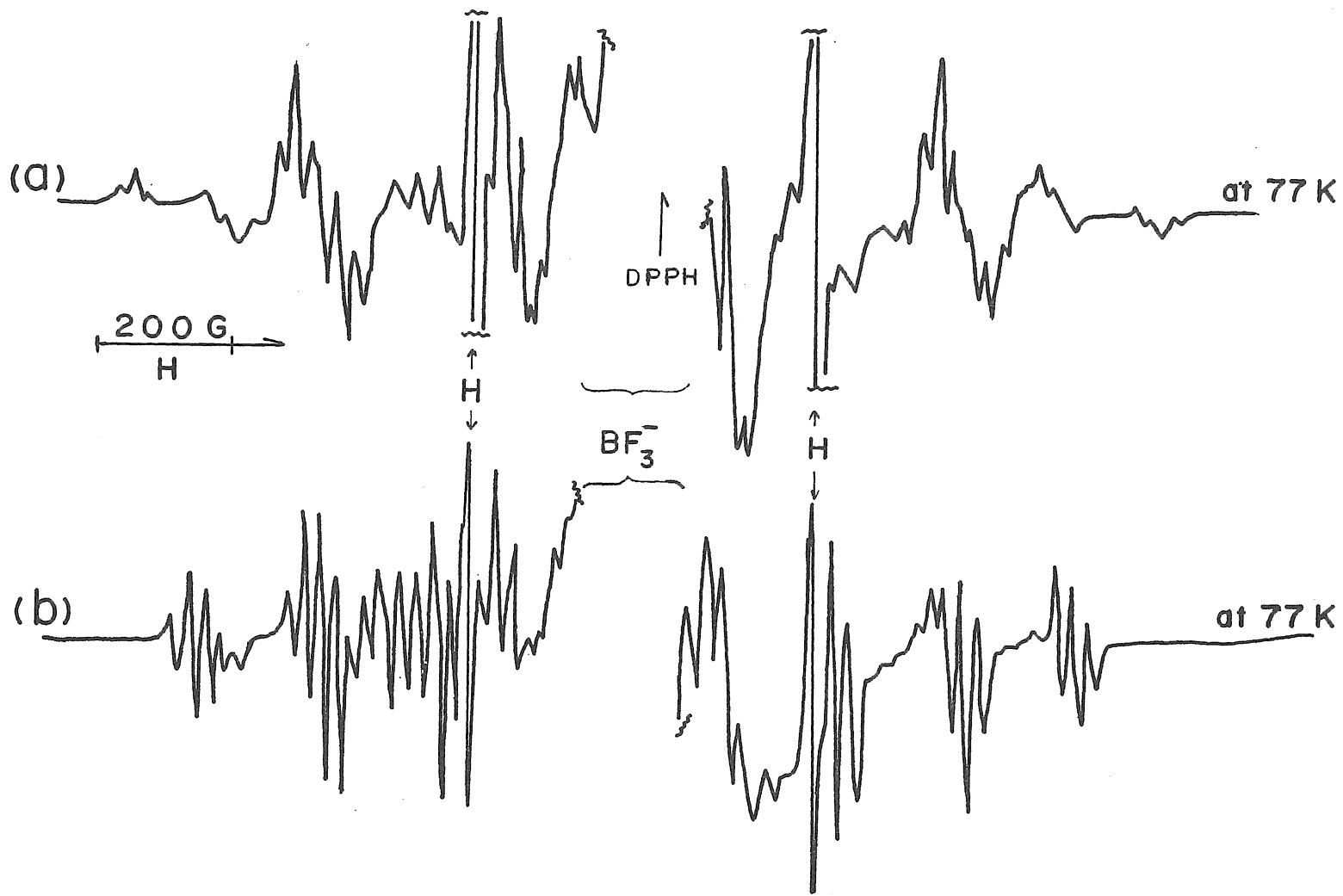


Fig. 1 ESR spectra of γ -irradiated (a) polycrystal and (b) single crystal of BF_3 .

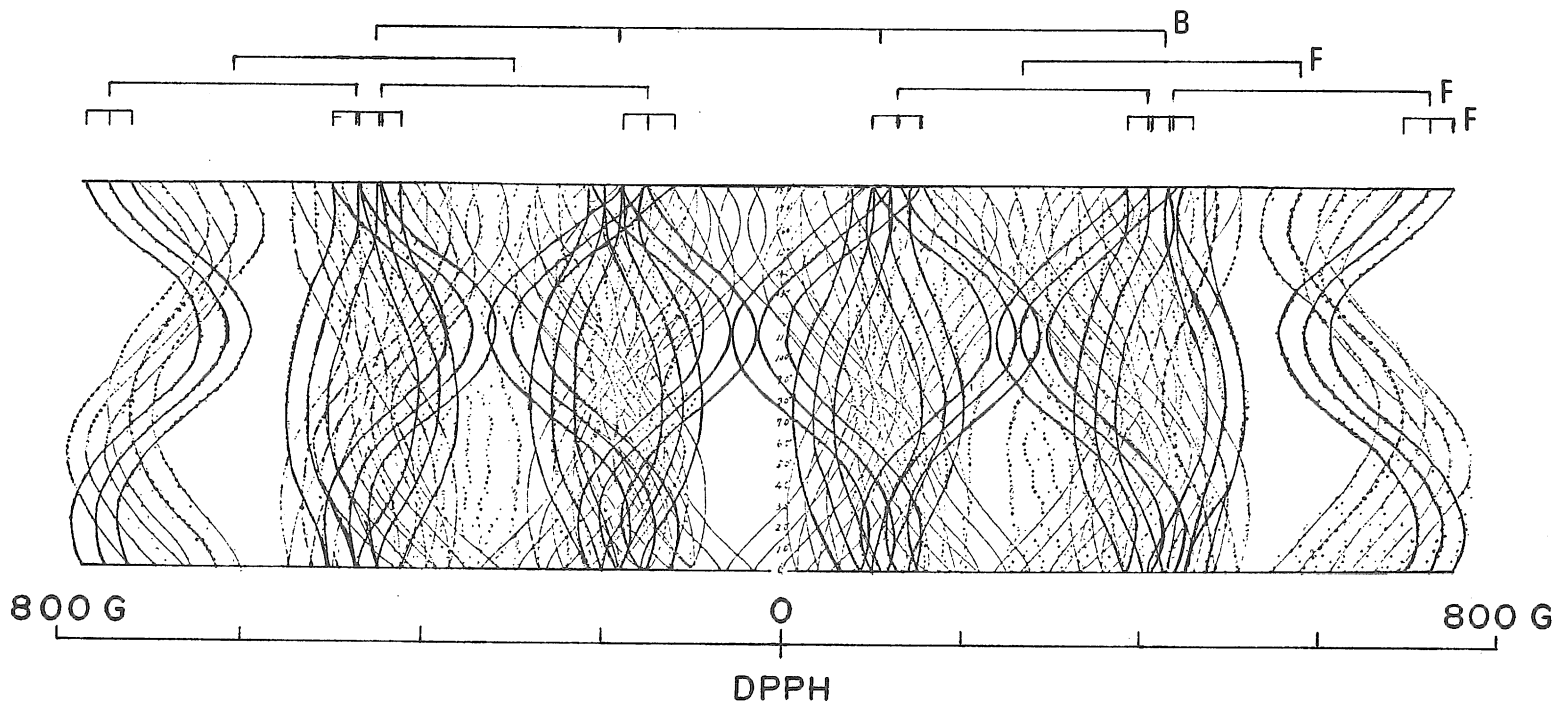


Fig. 2 Angular dependence of the spectral lines for the rotation about the crystal growth axis.

lar specimen. The angular dependence of the spectrum was measured by rotating the single crystal about the axis of the crystal growth, which is kept perpendicular to the external field. Spectra of two arbitrary orthogonal axes perpendicular to that of crystal growth were measured similarly.

RESULTS AND DISCUSSION

An ESR spectrum of a γ -irradiated polycrystal of BF_3 is shown in Fig. 1(a). This spectrum represented a pattern owing to an anisotropy characteristic of a solid state and consisted of weak signals having a large total spread of *ca.* 1500 G and intense signals with a total linewidth of *ca.* 200 G. The intense signals were interpreted to result from a BF_3^- radical since the BF_3^- radical might be produced by an electron capture of a BF_3 molecule under γ -irradiation. The BF_3^- radical was previously reported to be a π -radical with a $2P_z$ orbital occupied by an unpaired electron and with a total spread of 200 G¹⁾ and so was put away in this paper. The weak signals showed the same behaviors to the microwave power saturation and were interpreted to consist in the only radical species.

The weak signals were, however, unibisymmetric in the vicinity of signals of a hydrogen atom and this unibisymmetry might be caused by effects of a second-order perturbation which were often observed in the cases of the nucleus with a nuclear spin more than $I = 1$.⁹⁾ In this case, a B nucleus ($I = 3/2$) being able to expect the second-order perturbation and/or two F nuclei ($I = 1/2$) are involved and then the radical obtained here would be a boron-centered radical. This spectrum is, therefore, consist of four groups, in which each group is composed of a triplet with fairly large anisotropies. Furthermore, each component of the triplet is assumed to contain three lines with a line separation of *ca.* 25 G, as seen from bothside parts of the spectrum.

To further identify this radical species, an ESR spectrum of a γ -irradiated single crystal of BF_3 is similarly observed and is shown in Fig. 1 (b). In addition to the intense signals arised from the BF_3^- radical, the weak signals resulted from the boron-centered radical were also obtained with a conciseness and an increased intensity. This spectrum is

interpreted to be split into four groups by the B nucleus having the effects of the second-order perturbation and each group is composed of a triplet with a component splitting of *ca.* 200 G by two equivalent fluorine nuclei. The triplet is further subdivided to a triplet with relative intensities of 1 : 2 : 1 and with a coupling of *ca.* 25 G, as seen from the comparison with Fig. 1 (a). In this spectrum, two kinds of the triplets are considered to be formed by two equivalent fluorine nuclei, respectively.

A perfect analysis of a radical would be carried out by measurements of angular dependences of single crystal and so the angular dependences about the three mutually perpendicular axes of the γ -irradiated single crystal of BF_3 were measured. However, the analyses of the two orthogonal axes but the crystal growth axis could not carry out in spit of many attempts. The only result of the angular dependences around the axis of the crystal growth was shown in Fig. 2. There are three magnetically different sites, as seen readily from Fig. 2 and an existence of these three sites is reasonable under a consideration of a planar structure with a C_{3v} symmetry of the BF_3 molecule.¹⁰⁾ In each site, the triplet found in the outside parts exhibits the component splitting of 25 G, extending over all fields variations and is considered to consist in two equivalent fluorine nuclei with no anisotropy. The boron-centered radical is, therefore, identified to involve the B nucleus and two pairs of two equivalent fluorine nuclei.

In order to know a contribution of a second-order terms in hyperfine splitting of the B nucleus, calculations of resonance fields for the B nucleus were carried out by the second-order perturbation theory.⁹⁾ The transition $(M, m) \leftrightarrow (M-1, m)$ in the energy of the state (M, m) is determined as follow :

$$h\nu = g\beta H + A_m \{1 + (A_{\parallel}A_{\perp}^2/2A^2G)(2M - 1)\} + (A_{\parallel}^2 + A_{\perp}^2)(A_{\perp}^2/4A^2G) \{I(I + I) - m^2\} + \{(A_{\parallel}^2 - A_{\perp}^2)^2/8A^2G\} (g_{\parallel}g_{\perp} / g^2)^2 \sin^2 2\theta m^2$$

where, $G = g\beta H$

The contribution of the second-order terms was 25 G in these spectra and its value could explain the unibisymmetry found in these spectra reasonably. Then, the ESR parameters estimated here as follow :

Table 1 Comparison of the observed with thecalculated spin densities on the BF_2 radical.

Structure	^{11}B		^{19}F	
	ρ_{2s}	a_{2s} (G)	ρ_{2s}	a_{2s} (G)
Observed				
R = —, $\theta = 56^\circ$ ²⁾	0.410	295	0.011	190
Calculated				
R = —, $\theta = \text{—}$ ⁶⁾	0.476	343	0.010	172
R = 1.3 Å, $\theta = 56^\circ$	0.469	338	0.006	103
R = 1.3 Å, $\theta = 62^\circ$	0.449	323	0.009	155

$a_B = 295$ G, $a_F = 190$ G, and $a_F = 25$ G

These values are in good agreement with those of the BF_2 radical reported by Nelson and Gordy²⁾ except for $a_F = 25$ G.

The radical obtained here is interpreted to be very similar in structure with the BF_2 radical reported by Nelson and Gordy²⁾ because of having similar ESR parameters. Then, it is necessary to reexamine the spin densities of the BF_2 radical by the INDO-UHF method before the INDO-UHF method is adapted to the calculation of the spin densities on the radical in order to determine the structure of the boron-centered radical. A bond length of 1.3 Å from the data reported by an electron diffraction¹¹⁾ and the bond angle deduced from the ESR parameters²⁾ were used, respectively.

The results on the spin densities calculated by the INDO-UHF method are summarized in Table 1, together with the result reported by Zaucer and Azman,⁶⁾ and these values are fairly agreed with those estimated from the ESR parameters.²⁾ As the results in Table 1 show, the bond angle of $\theta = 62^\circ$ rather than $\theta = 51^\circ$ should be evaluated to obtain the best fit between the observed and calculated spin densities. Further agreements between the observed and calculated values might be expected by making use of a value, $R = 1.4$ Å, as the bond length of the BF_2 radical but no calculations were carried out. By the use of the INDO-UHF method giving the good results of the spin densities on the BF_2 radical, the spin densities on the boron-centered radical would be calculated and then the structure of

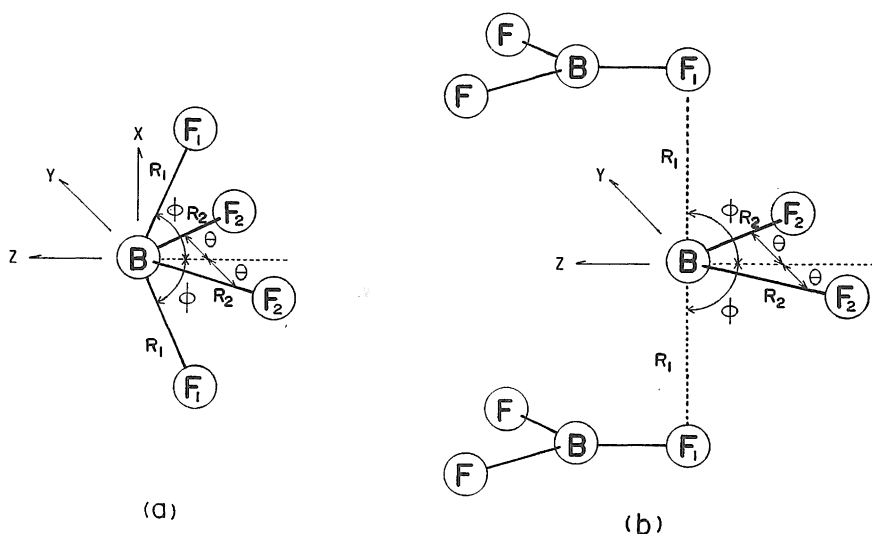


Fig. 3 The structure models for (a) the BF_4 radical and (b) the long-range interaction of the BF_2 radical with the nearest neighboring molecules.

the radical would be determined.

The PF_4 radical was well known to be the structure with two pairs of two equivalent fluorine atoms and with the bond angles of $\theta = 51^\circ$ and $\phi = 90^\circ$,^{8,12)} respectively. The boron-centered radical also contains two pairs of two equivalent fluorine atoms and then it may be a BF_4 radical with the same structure as the PF_4 radical. The model for the structure of the BF_4 radical is shown in Fig. 3 (a), using the same definitions as the PF_4 radical.¹²⁾

The results of the calculations on the spin densities for the BF_4 radical are summarized in Table 2. As the results in Table 2 show, the spin densities on the B nucleus slightly increase with the increases of the bond angle, θ , and/or the bond lengths, R, but are made no comparison with those estimated from the ESR spectrum. Furthermore, the spin densities on the F_2 nucleus increase with the increase of the bond angle, θ , but decrease with the increase of the bond angle, ϕ , in the case of $R_1 = R_2 = 1.3 \text{ \AA}$, while they become

in contrast with the results above in the case of $R_1 = R_2 = 1.4 \text{ \AA}$. The spin densities on the F_1 nucleus decrease with the increases of the bond angles of θ and ϕ and of the bond length of R_1 and R_2 , but they are larger than those on the F_2 nucleus except for the cases of $\phi = 87^\circ$ and $R_1 = R_2 = 1.4 \text{ \AA}$. Accordingly, it is found that the boron-centered radical is unsuccessfully explained by the model of the BF_4 radical with two pairs of two equivalent fluorine atoms, in any cases of the combinations of θ , ϕ , and R.

The spin densities of the two equivalent fluorine atoms having a small coupling of 25 G are only 0.0015 ($\rho = 0.15\%$), and the anisotropies owing to these fluorine atoms are hardly found, as seen from Fig. 2. Therefore, the coupling of 25 G is expected to result from the interactions between the ejection electron and the nearest neighboring two fluorine atoms because such long-range interactions are often seen in the studies on the single crystals irradiated at low temperature.⁸⁾ The model of the long-range interaction for

Table 2 The spin densities on the BF_4 radical calculated using the INDO method

Structure	Orbital	^{11}B	$^{19}\text{F}_2$ (two equivalent)		$^{19}\text{F}_1$ (two equivalent)	
$R_1 = R_2 = 1.3 \text{ \AA}$ $\theta = 51^\circ$	$\phi = 90^\circ$	S	-0.0235	0.0033	0.0034	
		P	-0.0390	0.3315	0.1931	
	$\phi = 110^\circ$	S	-0.0518	-0.0011	0.0015	
		P	-0.1021	0.3249	0.2517	
$R_1 = R_2 = 1.3 \text{ \AA}$ $\theta = 56^\circ$	$\phi = 80^\circ$	S	-0.0434	0.0026	0.0075	
		P	-0.1011	0.2747	0.2864	
	$\phi = 87^\circ$	S	-0.0498	0.0004	0.0049	
		P	-0.1046	0.2939	0.2780	
	$\phi = 110^\circ$	S	-0.0522	-0.0010	0.0016	
		P	-0.1011	0.3084	0.2676	
$R_1 = R_2 = 1.3 \text{ \AA}$ $\theta = 60^\circ$	$\phi = 80^\circ$	S	-0.0414	0.0030	0.0071	
		P	-0.0970	0.2709	0.2882	
	$\phi = 87^\circ$	S	-0.0498	0.0009	0.0047	
		P	-0.1034	0.2845	0.2865	
$R_1 = R_2 = 1.4 \text{ \AA}$ $\theta = 56^\circ$	$\phi = 80^\circ$	S	-0.0676	-0.0011	0.0027	
		P	-0.1365	0.3081	0.2924	
	$\phi = 87^\circ$	S	-0.0712	-0.0023	0.0010	
		P	-0.1330	0.3178	0.2856	
$R_1 = R_2 = 1.4 \text{ \AA}$ $\theta = 60^\circ$	$\phi = 80^\circ$	S	-0.0672	-0.0008	0.0024	
		P	-0.1357	0.3011	0.2987	
	$\phi = 87^\circ$	S	0.0710	-0.0021	0.0010	
		P	0.1322	0.3073	0.2954	

Table 3 The effects of the variations of the distance between the BF₂ radical and the nearest neighboring fluorine atom on the spin densities

Structure	Orbital	¹¹ B	¹⁹ F ₂ (two equivalent)	¹⁹ F ₁ (two equivalent)	
R ₂ = 1.3 Å θ = 56° φ = 90°	R ₁ = 1.5 Å	S	-0.4017	-0.0003	-0.0186
		P	-0.3446	-0.0227	-0.0853
	R ₁ = 2.0 Å	S	-0.4298	-0.0030	-0.0057
		P	-0.3374	-0.0522	-0.0556
	R ₁ = 2.5 Å	S	-0.4540	-0.0051	-0.0012
		P	-0.3347	-0.0739	-0.0254
	R ₁ = 2.8 Å	S	-0.4639	-0.0057	-0.0004
		P	-0.3355	-0.0809	-0.0130

Table 4 The effects of the variations of the bond angle of the BF₂ radical on the spin densities

Structure	Orbital	¹¹ B	¹⁹ F ₂ (two equivalent)	¹⁹ F ₁ (two equivalent)	
R ₁ = 2.5 Å R ₂ = 1.3 Å φ = 90°	θ = 51°	S	-0.4630	-0.0037	-0.0013
		P	-0.3255	-0.0699	-0.0308
	θ = 56°	S	-0.4540	-0.0051	-0.0012
		P	-0.3347	-0.0739	-0.0254
	θ = 60°	S	-0.4436	-0.0065	-0.0012
		P	-0.3450	-0.0772	-0.0208
	θ = 65°	S	-0.4280	-0.0087	-0.0011
		P	-0.3551	-0.0790	-0.0158
R ₁ = 2.8 Å R ₂ = 1.3 Å φ = 90°	θ = 51°	S	-0.4735	-0.0043	-0.0005
		P	-0.3281	-0.0775	-0.0170
	θ = 56°	S	-0.4639	-0.0057	-0.0004
		P	-0.3355	-0.0809	-0.0130
	θ = 60°	S	-0.4530	-0.0073	-0.0004
		P	-0.3439	-0.0836	-0.0103
	θ = 65°	S	-0.4372	-0.0095	-0.0004
		P	-0.3509	-0.0864	-0.0071

the boron-centered radical is shown in Fig. 3 (b), on the assumptions that the bond length, R₁, refers to the distance between the BF₂ radical and the nearest neighboring fluorine atom and the unpaired electron is in a straight line with the two fluorine atoms. The plane of the BF₂ radical, yz plane, is mutually orthogonal with the one containing the nearest neighboring fluorine atoms, xz plane.

The spin densities for the model of the long-range interaction are calculated by the INDO-UHF method and effects of variations of R₁ on the spin densities are tabulated in Table 3. As the summary in Table 3 shows, both spin densities on the B and F₂ nuclei

increase with the increase of R₁, while the spin densities on the F₁ nucleus decrease: this is because the probability of the electron ejecting to the F₁ nucleus decreases as the distance increases. All results are satisfactorily obtained. The distance between the BF₂ radical and the nearest neighboring two fluorine atoms may be in order of 2.5 to 2.8 Å, because the spin densities on the F₂ nucleus in the case of R₁ = 2.0 Å are too small in spite of the most suitable value of all spin densities on the B nucleus.

In determining the optimum geometry, the total energy was first minimized with respect to the distance, R₁, and then with the distance fixed, the bond angle was optimised.

The effects of variations of the bond angle, θ , on the spin densities in the cases of $R_1 = 2.5$ and 2.8 \AA are tabulated in Table 4. As the summary in Table 4 also shows, the spin densities on the B nucleus decrease with the increase of the bond angle, θ , and the decrease of the distance, R_1 , while the spin densities on the F_2 nucleus increase with the increases of the bond angle and the distance.

From these results, the structure with the bond angle of $\theta = 65^\circ$ and the distance of $R_1 = 2.8 \text{ \AA}$ might be favorable for the boron-centered radical but a question is raised whether the bond angle of the BF_2 radical becomes larger than that of the BF_3 molecule.

Many calculations⁷⁾ exhibited the bond angle of the BF_2 radical to be 130° or less, assuming that the stretching and bending force constants were the same as for BF_3 . It is natural to yield the best fit in the case of

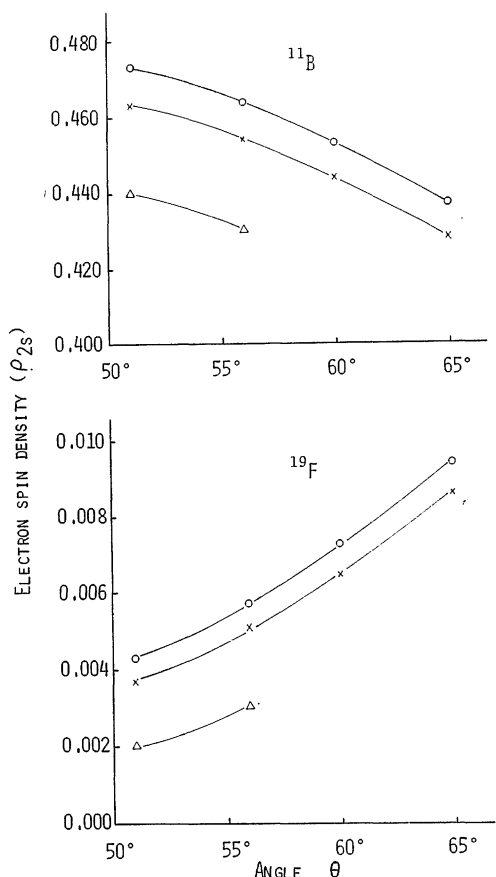


Fig. 4 The variations of the spin densities on the B and F_2 nuclei with the bond angle of the BF_2 radical. — Δ — ; $R_1 = 2.0 \text{ \AA}$, — \times — ; $R_1 = 2.5 \text{ \AA}$, — \circ — ; $R_1 = 2.8 \text{ \AA}$.

$\theta = 65^\circ$ because the INDO-UHF calculations were carried out in this article, on the basis of such the assumption. The bond angle of the BF_2 radical was deduced to be 112° from the analysis of the analysis of the ESR spectrum²⁾ and so the bond angle of the BF_2 radical obtained here is much the same as 112° . Also, the bond length, R_2 , in the BF_2 radical is expected to become slightly longer than that of the BF_3 molecule to keep the balance of the geometry and may extend to 1.4 \AA .

To summarize the results in Tables 3 and 4, the relationship between the spin densities and the bond angle, θ , is derived and is shown in Fig. 4. It is found in this figure that increasing the bond angle or decreasing the distance tends to decrease the spin densities on the B nucleus and to increase the ones on the F_2 nucleus. In both cases of the distance of $R_1 = 2.5$ and 2.8 \AA , the spin densities on the B and F_2 nuclei approach the observed values as the bond angles, θ , become larger, respectively. However, as mentioned above, the bond angle of the BF_2 radical ought to become shorter than that of the BF_3 molecule, while the bond length ought to do longer than that of the BF_3 molecule. Apparently from the results in Table 1 and Fig. 4, the value of the bond length, $R_2 = 1.4 \text{ \AA}$, offers the best fit results for the structure of the BF_2 radical and the distance between the BF_2 radical and the nearest neighboring fluorine atom, $R_1 = 2.8 \text{ \AA}$ (just twice as the bond length of $R_2 = 1.4 \text{ \AA}$) is suitable for explaining the long-range interaction. Accordingly, the BF_2 radical produced in the irradiated single crystal of BF_3 may be the structure with the bond angle of *ca.* 112° and the bond length of *ca.* 1.4 \AA , and may interact with the nearest neighboring two fluorine atoms in the two BF_3 molecule being *ca.* 2.8 \AA from the BF_2 radical.

The study like this, though being failed to analysis perfectly the structure of the BF_2 radical, can be extended to as many molecules with no X-rays data as are need to obtain some informations about the molecular packing, the relative orientations of the surrounded molecules, and so on.

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