

$d^i$  refers to the  $-x, -y, -z$  symmetry position and  $d^{2i}$  to that of  $-x, 1-y, -z$ ;  $b/2$  is equal to 3.848 Å. Further short contacts are established between O(3) and the ethyl C atom C(11'<sup>2i</sup>)[3.215 (8) Å] as well as between O(3) and one of the ethyl H atoms H(11'<sup>32i</sup>) [2.44 (6) Å].

Within the centrosymmetric pair the molecules are laterally displaced with respect to each other. If the molecular long axis is taken along the methinic chain and the aggregate axis, the vector connecting the midpoints ( $A$ ) of the C(3)–C(4) bonds, the slip angle  $C(4) \cdots A \cdots A^i$  is 55°.

The molecular stacks are crosslinked through the following short contacts:

	$d$ (Å)		$d$ (Å)
O(1)···C(9 <sup>4i</sup> )	3.362 (8)	O(2)···S(1' <sup>3i</sup> )	3.101 (4)
O(1)···S(1' <sup>3i</sup> )	3.203 (4)	C(9)···C(11' <sup>4i</sup> )	3.794 (8);
O(1)···H(7' <sup>3i</sup> )	2.45 (4)		

3i and 4i correspond to  $x, \frac{1}{2} - y, \frac{1}{2} + z$  and  $-x, \frac{1}{2} + y, \frac{1}{2} - z$  symmetry operations respectively.

### Conclusion

In the solid state the polar zwitterionic mesomeric form of the merocyanine is dominant. The molecular geometry of the thiazole ring approaches that of the thiazolium cation and the phenolate ring is the negatively charged moiety of the molecule. The presence of the electron-withdrawing  $NO_2$  substituent in the phenolate ring enhances the delocalization of the negative charge

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## Structure of 1-Fluoroadamantane, $C_{10}H_{15}F$ , in its Plastic Phase

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### Abstract

Single-crystal X-ray diffraction data were collected and interpreted for the plastic phase of 1-fluoroadamantane,  $C_{10}H_{15}F$  at 293 K. The unit cell is face-centred cubic with  $a = 9.535$  (4) Å, space group  $Fm\bar{3}m$ ,  $Z = 4$ . On the assumption of a rigid molecular skeleton, several types of orientational disorder were

on this part of the molecule and contributes to the stabilization of the polar structure of the merocyanine.

We are indebted to Professor Y. Jeannin for his great interest in this investigation. Thanks are due to Drs M. Le Baccon for supplying the crystals and P. Toledano for the data collection.

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investigated: hindered reorientations between equally weighted orientations, free uniaxial rotation of the molecules about the C–F axis and decomposition of the atomic orientational average density on symmetry-adapted functions. With the first and the third models agreement between observed and calculated structure factors is found in which molecular (C–F) and lattice ( $[111]$ ) threefold axes are aligned.

## I. Introduction

1-Fluoroadamantane,  $C_{10}H_{15}F$ , formally known as 1-fluorotricyclo[3.3.1.1]decane, is a globular molecule (Fig. 1) of  $C_{3v}$  symmetry, obtained from adamantane ( $C_{10}H_{16}$ ) by replacing one methylene H by a fluorine atom. This substitution is of great interest in that it gives a dipole moment ( $7.037 \times 10^{-30}$  Cm) to the molecule along the C–F axis (Deady, Kendall, Topsom & Jones, 1973).

The NMR and dielectric relaxation experiments we performed (Amoureux, 1980) had proved that, like adamantane, fluoroadamantane is a plastic crystal at room temperature between the transition temperature ( $T_t = 221.6$  K) and the melting point ( $T_m = 525$  K) (Clark, Knox, Mackle & Hervey, 1977).

Owing to the existence of orientational disorder, classical methods could not be used. This compound was thus studied using the two structure determination procedures we have already described (Amoureux & Bee, 1979; Amoureux, Sauvajol & Bee, 1981).

## II. Structure with a Frenkel model of a plastic crystal made of rigid molecules

The main hypothesis is that the substitution of a methylene hydrogen by a fluorine atom does not distort the rest of the molecule. All the atoms are totally defined in a coordinate system fixed in the molecule and rotating with it (Fig. 1). Next, this molecular coordinate system has to be put in a general position with respect to the crystal lattice built up from the centres of gravity of the averaged molecules. For this we first need to relate the origin of the molecular axes to that of this crystal lattice by an eccentricity vector  $\mathbf{e}$ , which must be for symmetry considerations along the threefold axis of the molecule (C–F). Then we must rotate the molecular axes with respect to the crystal lattice by the so-called Euler angles  $(\alpha, \beta, \gamma)$ . If  $(\alpha, \beta, \gamma)$  defines one

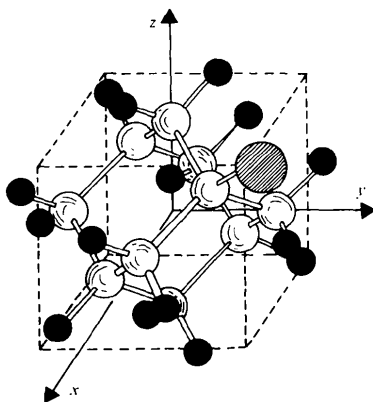


Fig. 1. Molecule of  $C_{10}H_{15}F$  defined in a set of orthonormal axes referred to the centre of mass of the tertiary C atoms.

equilibrium position for the molecule, the others will be obtained by applying the symmetry operations of the site group for the time-averaged crystal. We thus obtain 48 equilibrium positions for a particular molecule in one general position if the site group is  $m\bar{3}m$  and only 24 if it is  $\bar{4}3m$  or  $432$ .

We have used the weighted reliability factor  $R_w$  and the molecular parameters already described (Amoureux & Bee, 1979).

The distance between the fluorine atom and the centre of mass of the four tertiary carbons has the following value:  $R_{FT} = 2.90$  Å.

### 1. Temperature factor: $\exp(-W)$

With the shape of the molecule taken into account one can define two different anisotropic rotational and translational Debye–Waller factors which respectively represent:

$\langle \theta_{\parallel}^2 \rangle$  the librations of the molecule around its threefold axis C–F

$\langle \theta_{\perp}^2 \rangle$  the librations perpendicular to this dipolar axis

$\langle u_{\parallel}^2 \rangle$  the translations along the C–F axis

$\langle u_{\perp}^2 \rangle$  the translations along any axis perpendicular to the first one.

The translational mean-square amplitude  $\langle u^2 \rangle$  can then be defined:

$$\langle u^2 \rangle = \langle u_{\parallel}^2 \rangle + 2 \langle u_{\perp}^2 \rangle. \quad (1)$$

It can be seen (Amoureux, 1980) that to a first-order approximation we have:

$$W/2\pi^2 = X_{\parallel}^2 \langle u_{\parallel}^2 \rangle + X_{\perp}^2 \langle u_{\perp}^2 \rangle$$

$$+ (\mathbf{X} \times \mathbf{M})_{\parallel}^2 \langle \theta_{\parallel}^2 \rangle + (\mathbf{X} \times \mathbf{M})_{\perp}^2 \langle \theta_{\perp}^2 \rangle, \quad (2)$$

where  $\mathbf{M}$  is the vector joining each atom to the origin of the crystal lattice,  $\mathbf{X}$  is the vector of diffusion, and  $X_{\parallel}$ ,  $(\mathbf{X} \times \mathbf{M})_{\parallel}$ ,  $X_{\perp}$  and  $(\mathbf{X} \times \mathbf{M})_{\perp}$  are the components of  $\mathbf{X}$  and  $\mathbf{X} \times \mathbf{M}$  respectively along and perpendicular to the molecular threefold axes.

When thermal motions are isotropic, one can define two isotropic mean-square amplitudes:

$$\langle \theta_{\parallel}^2 \rangle = \langle \theta_{\perp}^2 \rangle = \langle \theta^2 \rangle$$

$$\langle u_x^2 \rangle = \langle u_{\parallel}^2 \rangle = \langle u_{\perp}^2 \rangle = \langle u^2 \rangle / 3. \quad (3)$$

Then (2) can be simplified and gives the ‘classical’ approximation of Willis & Pawley (1970)

$$W/2\pi^2 = X^2 \langle u_x^2 \rangle + (\mathbf{X} \times \mathbf{M})^2 \langle \theta_{\parallel}^2 \rangle. \quad (4)$$

### 2. Free uniaxial rotation

For such a model the scattering function is

$$\exp(-W) f(X) \exp[2i\pi \mathbf{M}_0 \times \mathbf{X}] J_0(2\pi r) \quad (5)$$

(*International Tables for X-ray Crystallography*, 1959), where  $f(X)$  is the atomic X-ray scattering factor

(in electrons),  $t$  in reciprocal space is the distance from  $\mathbf{X}$  to an axis parallel to the axis of rotation and passing through the origin,  $\mathbf{M}_0$  is the projection of the  $\mathbf{M}$  vector on the axis of free rotation,  $J_0$  is the zeroth-order cylindrical Bessel function, and  $r$  is the distance between the atom and the axis of rotation.

In this model, only the librations perpendicular to the axis of free rotation with mean-square amplitude  $\langle \theta_1^2 \rangle$  have to be taken into account for the temperature factor. Therefore, one has only to fix  $\langle \theta_2^2 \rangle = 0$  in (2).

### III. Symmetry-adapted function analysis of plastic crystals

In this method (Amoureux, Sauvajol & Bee, 1981), the coupling between translational and rotational motions is neglected. Therefore the structure factor  $F(\mathbf{X})$  can be written as a product of two terms: the first one corresponds to the centre-of-mass translations and the second to the librations. As we deal with cubic symmetry, we use an isotropic translational Debye–Waller factor:

$$F(\mathbf{X}) = \exp[-2\pi^2 X^2 \langle u_x^2 \rangle] F^{\text{rot}}(\mathbf{X}).$$

The second term (rotational form factor), for a molecule with atoms arranged in  $s$  shells with  $n_\mu$  equivalent atoms in the  $\mu$ th shell, can be written in X-ray diffraction as:

$$F^{\text{rot}}(\mathbf{X}) = \sum_{l,m,m'} i^l A_{mm'}^l T_{m'}^l(X) L_{l,m}(\Omega_{\mathbf{X}}) \quad (6)$$

with

$$T_{m'}^l(X) = 4\pi \sum_{\mu=1}^s j_l(2\pi X R_\mu) b_{l,m'}^\mu n_\mu f_\mu(X). \quad (7)$$

$R_\mu$  is the radius of the  $\mu$ th shell,  $j_l$  is the spherical Bessel function of order  $l$ , and  $b_{l,m'}^\mu$  can be calculated from the atomic positions (Press & Huller, 1973). In (6) the lattice symmetry gives the  $L_{l,m}$  functions and the molecular symmetry influences the  $T_{m'}^l(X)$  terms by means of the  $b_{l,m'}^\mu$ . The time-averaged orientation of the molecule in the lattice is given by the  $A_{mm'}^l$  which are introduced as parameters in the refinements.

For fluoroadamantane, the orientational average density  $C_F(\theta, \varphi)$  with respect to the cubic lattice of the C–F axis is fixed by the terms  $A_{m1}^l$  alone and the functions  $L_{l,m}$  are then the classical cubic harmonics  $K_{l,m}$  (Amoureux *et al.*, 1981)

$$C_F(\theta, \varphi) = \sum_{l,m} A_{m1}^l \left( \frac{2l+1}{4\pi} \right)^{1/2} K_{l,m}(\theta, \varphi). \quad (8)$$

Therefore, the  $A_{mm'}^l$  terms can be separated into two groups:

the  $A_{m1}^l$ , which fix the orientational average density of the molecular threefold axis;

the other terms  $A_{mm'}^l$  ( $m' \neq 1$ ) which determine the molecular position around the dipolar axis. These terms are all equal to zero for a free uniaxial rotation around this C–F axis.

### IV. Experiment

1-Fluoroadamantane was prepared from 1-bromoadamantane (Fort & Schleyer, 1965) and the purity of this compound was verified by chromatography. Measurements were made at room temperature on an automatic X-ray diffractometer (Philips PW 1100) with Mo  $K\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) and a 0.8 mm  $\varnothing$  collimator. To avoid free sublimation, the single crystal (size  $\approx 0.5$  mm) was sealed in a glass capillary tube. A  $\theta$ – $2\theta$  scan with a minimum speed of  $0.008^\circ \text{ min}^{-1}$  and a fixed scan width of  $1.4^\circ$  was used.

In order to be sure that secondary extinction did not occur a comparison of strong reflections for two single crystals very different in size was performed. Within 3% the experimental intensities were always in the same ratio for the two crystals and hence no absorption or extinction corrections were applied. In this plastic crystal the number of independent observed reflexions is very small (116) and only 52 of them correspond to  $F_o/\sigma \geq 3$ .

The condition  $F_o(hkl) = F_o(\bar{k}hl)$  has always been verified by diffractometer measurements. This point has allowed us to reject the  $Fm3$  and  $F23$  groups, leaving only three possibilities:  $Fm3m$ ,  $F\bar{4}3m$  and  $F432$ .

### V. Structure determination with a Frenkel model

#### 1. 'Equilibrium positions'

Whatever the site group ( $m3m$ ,  $\bar{4}3m$  or  $432$ ) the lowest  $R_w$  values were found for  $\alpha, \beta, \gamma$  and  $e$  nearly equal to zero. For this special position ( $\alpha = \beta = \gamma = e = 0$ ), the  $m3m$  factor group gives eight distinct 'equilibrium positions' and the  $\bar{4}3m$  and  $432$  groups the same four.

The refinements with an isotropic temperature factor have given for these 'equilibrium positions':

$$Fm3m, R_w = 9.4\%, \langle u_x^2 \rangle = (0.061 \pm 0.002) \text{ \AA}^2, \\ \langle \theta_1^2 \rangle^{1/2} = (8.0 \pm 0.2)^\circ \quad (9)$$

$$F\bar{4}3m, F432, R_w = 31.8\% \langle u_x^2 \rangle = (0.045 \pm 0.008) \text{ \AA}^2, \\ \langle \theta_1^2 \rangle^{1/2} = (9.2 \pm 0.6)^\circ.$$

A comparison of the two  $R_w$  values allows us to conclude that fluoroadamantane crystallizes in  $Fm3m$  with eight 'equilibrium positions'.

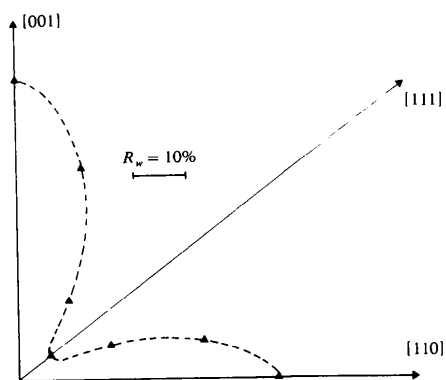


Fig. 2. Minimum  $R_w$  values versus the position of the F atom, for different mean orientations corresponding to a rotation around the  $[1\bar{1}0]$  axis. These results are to be related to  $\langle \theta_{\perp}^2 \rangle^{1/2} = 6.5^\circ$ . The  $R_w$  value is proportional to the distance of one of the points on the curve to the origin. The length corresponding to  $R_w = 10\%$  is marked.

When the parameters  $\alpha$ ,  $\beta$  and  $\gamma$  are left free to vary about this special position, we then obtain our best fit ( $R_w = 8.5\%$ ) for molecules with the C–F bond  $2.2^\circ$  away from the  $[111]$  axes. We think that this result has no real physical meaning: improvement in  $R_w$  is obtained only because three new fitting parameters ( $\alpha$ ,  $\beta$  and  $\gamma$ ) are used.

We have made another test on the accuracy of ‘equilibrium-position’ determination. In Fig. 2, we report for the  $Fm\bar{3}m$  space group, the minimum  $R_w$  value versus the position of the F atom.

We have seen that the refinements have located the origin of the crystal lattice at the centre of mass of the four tertiary C atoms ( $e = 0$ ) and not at that of the molecule ( $e = 0.34 \text{ \AA}$ ). Fig. 3 shows the  $R_w$  minimum versus  $e$  for a few values of this parameter. Fig. 4 shows the packing and explains quite well the zero value of the eccentricity parameter  $e$ . Indeed, we can

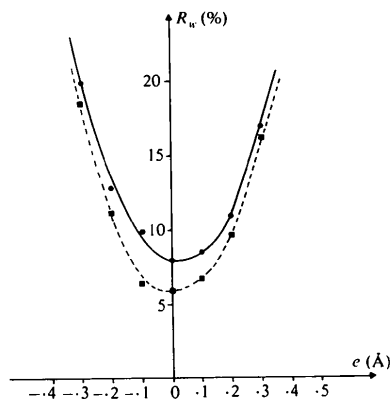


Fig. 3. Minimum  $R_w$  value versus the eccentricity parameter  $e$  ( $\text{\AA}$ ). The circles are for the Frenkel model and the squares for the second method.

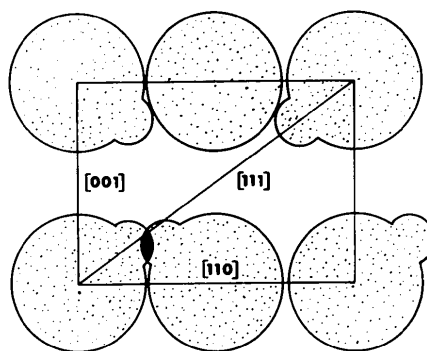


Fig. 4. Example of packing in the  $(1\bar{1}0)$  plane. The black zone corresponds to the steric hindrance.

see that the spheres, on which H atoms are located, are all in contact, therefore fixing the  $e$  parameters at zero.

## 2. Anisotropic thermal factor

If we take into account the shape of the molecule and the cubic lattice, two different types of motions can coexist in fluoroadamantane: a uniaxial rotation around the C–F axis and a tumbling isotropic reorientation of this dipole moment between the  $[111]$  axes. Preliminary incoherent quasi-elastic neutron scattering (IQNS) measurements (Bee, 1980) have shown that the first motion is faster than the second. Therefore we have assumed that the thermal motions can be anisotropic and we have carried out the refinements\* in the space group  $Fm\bar{3}m$  with the preceding fixed values  $\alpha = \beta = \gamma = e = 0$ ,

$$R_w = 8.0\%, \langle u_x^2 \rangle = (0.060 \pm 0.001) \text{ \AA}^2, \\ \langle \theta_{\parallel}^2 \rangle^{1/2} = (11.0 \pm 0.6)^\circ, \langle \theta_{\perp}^2 \rangle^{1/2} = (6.5 \pm 0.2)^\circ. \quad (10)$$

The refinements carried out with an anisotropic translational Debye–Waller factor did not change  $R_w$  and the thermal parameters ( $\langle u_{\parallel}^2 \rangle$ ,  $\langle u_{\perp}^2 \rangle$ ). We note that  $\langle \theta_{\parallel}^2 \rangle$  is greater than  $\langle \theta_{\perp}^2 \rangle$ . This confirmation of the existence of preferred reorientations persuaded us to try the free uniaxial rotational model described in II.2. The very bad consecutive agreement ( $R_w = 40\%$ ) allows us to conclude that the uniaxial rotation for the molecule is not free but strongly hindered. This hindered rotation is related to the fact that  $\langle \theta_{\parallel}^2 \rangle^{1/2} = 11^\circ$  is much lower than the angle of rotation ( $120^\circ$ ) around the C–F axis allowing the molecule to pass from one equilibrium position to another.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36750 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## VI. Structure determination with cubic harmonics

In order to verify the preceding results, we have also used the decomposition on cubic harmonic functions of the molecular orientational probability. We used the molecular parameters already described for a similar molecule:  $C_{10}H_{15}CN$  (Amoureux, Sauvajol & Bee, 1981). We first used a free isotropic rotational model ( $A_{mm'}^l = \delta_{l,0}$ ), but the agreement was very poor:  $R_w = 60\%$ . We secondly carried out a refinement in the  $Fm\bar{3}m$  space group ( $e = 0$ ), with a free uniaxial rotational model (only  $A_{m1}^{2p} \neq 0$ ). The corresponding  $A_{11}^{2p}$  values (Table 1) agree well with the molecular (C–F) and lattice ([111]) threefold axes aligned. However, the high  $R_w$  value ( $R_w = 33\%$ ) points out once more the fact that the molecular uniaxial rotation is not free but strongly hindered. We then had to modulate the molecular orientational probability around the dipolar C–F axis and then had to refine the other parameters  $A_{mm'}^{2p}$  ( $m' \neq 1$ ).

The signs and values of these terms vary considerably according to the molecular 'equilibrium positions'. We have therefore introduced, as initial  $A_{mm'}^l$  values in the refinements, those corresponding (Amoureux,

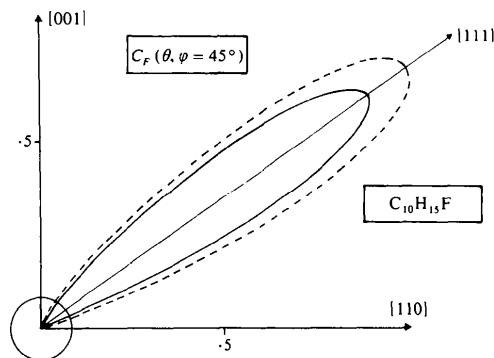


Fig. 5. The orientational average nuclear density in the  $(1\bar{1}0)$  plane for the C–F group. The dashed curve corresponds to the free uniaxial rotation ( $R_w = 33\%$ ) and the solid curve to the threefold uniaxial rotation ( $R_w = 6\%$ ). The circle corresponds to the value  $1/4\pi$  for a completely random distribution of orientations.

Sauvajol & Bee, 1981) to the 'equilibrium positions' deduced from the Frenkel model. These 'equilibrium positions' are obtained with the Euler angles ( $\alpha_1 = 45^\circ$ ,  $\beta_1 = 54.74^\circ$ ,  $\gamma_1 = 180^\circ$ ) which bring the dipole moment C–F along [111] and the secondary carbons along the [001] axes. We obtained excellent agreement ( $R_w = 5\%$ ) using too many parameters (24 up to order 12); we then set aside those which influenced  $R_w$  only a little.

During these trials to eliminate the parameters we established the fact that the  $A_{m1}^{2p}$  terms describing the orientational probability for the dipolar axis stayed always nearly constant. On the other hand, the other terms  $A_{mm'}^{2p}$  ( $m' \neq 1$ ) varied a lot (except for  $A_{12}^4$ ) from one trial to another. These variations are related to the fact that for each order  $l$  of the development of the molecular orientational probability around its C–F axis, this probability is a linear combination of several rotator functions whose coefficients  $A_{mm'}^l$  ( $m' \neq 1$ ) are correlated with each other except for order four where there exists only a single term  $A_{12}^4$ .

The orientational probability of the dipole moment (C–F) in the  $(110)$  plane (Fig. 5) shows well the fact that for the 'equilibrium positions' the molecular (C–F) and lattice [111] threefold axes are aligned. The molecular orientational probability around the dipolar axis C–F fixed along [111] is given by the following relation:  $f(\eta') = f(45^\circ, 54.74^\circ, 180^\circ + \eta')$ . We can see in Fig. 6, which represents  $f(\eta')$ , that the 'equilibrium positions'  $\eta' = 0$  ( $\pm 120^\circ$ ) correspond well to those deduced with the Frenkel model, that is to say with the six secondary carbons along the [001] axes. The librational r.m.s. amplitudes for the C–F axis  $\langle \theta_1^2 \rangle^{1/2} \simeq 7^\circ$  (Fig. 5) and around the C–F axis  $\langle \theta_0^2 \rangle^{1/2} \simeq 10^\circ$  (Fig. 6) have nearly the same values as those found with the Frenkel model (10). This preceding orientational probability  $f(\eta')$  presents a second maximum at  $60^\circ$  from the first one. This second maximum does not represent an 'equilibrium position' but is certainly related to the truncation, to the order 12, of the development of  $f(\eta')$  on the rotator functions. Thus for a fixed molecule without libration in  $\omega_1$ ,  $8\pi^2 f(\eta')$  always presents two maxima (Amoureux *et al.*, 1981, Fig. 5): the first at  $\eta' = 0^\circ$  and the second at

Table 1. Results for fluoroadamantane

The molecule fixed in  $\omega_1$ , without librations, corresponds also to  $A_{12}^6 = 0.54$ ,  $A_{12}^{10} = 0.12$ ,  $A_{13}^{10} = 0.45$ ,  $A_{11}^{12} = 0.06$ ,  $A_{12}^{12} = 0.48$ ,  $A_{14}^{12} = 0.69$ ,  $A_{22}^{12} = -0.44$ ,  $A_{23}^{12} = -0.61$ ,  $A_{24}^{12} = -0.08$ ,  $A_{25}^{12} = -0.50$ .

$R_w$ (%)	$\langle \mu_x^2 \rangle$ ( $\text{\AA}^2$ )	$A_{11}^4$	$A_{12}^4$	$A_{11}^6$	$A_{13}^6$	$A_{11}^8$	$A_{12}^8$	$A_{13}^8$	$A_{11}^{10}$	$A_{14}^{10}$	$A_{13}^{12}$	$A_{15}^{12}$	$A_{21}^{12}$
Molecule fixed in $\omega_1$		-0.51	0.86	0.63	0.56	0.21	-0.62	0.75	-0.65	0.60	-0.53	0.07	-0.41
39	0.010	-0.44		0.85		0.39							
33	0.015	-0.48		0.82		0.51			-0.26				
6	0.056	-0.30	0.66	0.52	0.48		-0.16	0.40	-0.33	0.50	-0.32	0.61	-0.25
	$\pm 0.002$	$\pm 0.02$	$\pm 0.02$	$\pm 0.02$	$\pm 0.03$		$\pm 0.04$	$\pm 0.02$	$\pm 0.02$	$\pm 0.12$	$\pm 0.08$	$\pm 0.14$	$\pm 0.02$

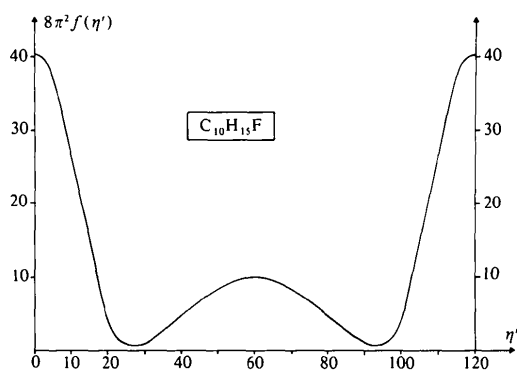


Fig. 6. Molecular orientational probability  $f(\eta')$ , the dipole moment is fixed on  $[111]$ .  $\eta' = 0$  corresponds to the secondary carbons along the  $[001]$  axes.

$\eta' = 60^\circ$ , whose values are respectively, for order 12, 111 and 15; for order 10, 61 and 11; and, for order 8, 40 and 6. We have then verified that the centres of gravity of the averaged molecule and of the four tertiary carbons are identical (Fig. 3). Finally, we also verified that the spatial group is centred ( $Fm\bar{3}m$ ) by introducing in the refinement  $A_{11}^3$  and  $A_{11}^1$  which stayed nearly equal to zero.

## VII. Discussion

We have analysed the structure of fluoroadamantane using two different methods: a Frenkel model and a decomposition of the molecular orientational probability on cubic harmonic functions. These two methods have given the same results: same 'equilibrium positions', same eccentricity parameter ( $e = 0$ ) and same amplitude for the thermal motions: isotropic for the translations and anisotropic for the librations.

The molecule has eight 'equilibrium positions' corresponding to the threefold axis C–F along the eight  $[111]$  lattice axes. Therefore, the ten carbons always have the same positions as in adamantane ( $C_{10}H_{16}$ ) and 2-adamantanone ( $C_{10}H_{14}O$ ) (Amoureux & Bee, 1980).

In this crystal, we have found two types of motions. The molecule can perform a threefold uniaxial rotation around the C–F axis and no steric hindrance then occurs. The molecular dipole moment stays fixed (Fig. 4) and therefore  $\langle \theta_{\parallel}^2 \rangle$  and the corresponding frequency [as verified in IQNS (Bee, 1980)] are large. On the other hand, by looking at Fig. 4, one can see that the C–F reorientations cannot occur without a huge local distortion of the crystal lattice. Therefore  $\langle \theta_{\perp}^2 \rangle$  and the corresponding frequency (Bee, 1980) are small. The negligible anisotropy for the translational thermal motions is certainly related to the quasi-isotropy of the molecular tensor of inertia.

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