

mation of 4,4'-difluorobiphenyl is mainly due to the modification of intramolecular potential by inductive and mesomeric effects or to the perturbation of packing forces, as is observed in biphenyl under pressure. This absence of any structural transition at low temperature shows 4,4'-difluorobiphenyl to be a very good candidate for studies of lattice dynamics for non-rigid molecules.

The authors gratefully thank Dr J. L. Baudour for the use of the WAGG program and for helpful discussions on thermal analysis.

Note added in proof: Recent calculations on the stability of the molecular geometry in 4,4'-difluorobiphenyl (Saito, Atake & Chihara, 1987) let us expect that the planar conformation is the most stable one at 0 K.

References

- ALMENNINGEN, A., BASTIANSEN, O., GUNDERSEN, S., SAMDAL, S. & SKANCKE, A. (1985). *J. Mol. Struct.* **128**, 95-114.
- BARRETT, R. M. & STEELE, D. (1972). *J. Mol. Struct.* **11**, 105-125.
- BAUDOUR, J. L. (1972). *Acta Cryst.* **B28**, 1649-1656.
- BAUDOUR, J. L., TOUPET, L., DÉLUGEARD, Y. & GHMID, S. (1986). *Acta Cryst.* **C42**, 1211-1217.
- BIELUSHKIN, A. V., NATKANIEC, I., WASICKI, J., KHOMENKO, V. G., TELEZHENKO, YU. V. & WASIUTYNSKI, T. (1986). 10th European Crystallographic Meeting, Wrocław, Poland, Collected Abstracts, 3A-05, pp. 350-351.
- BOLHUIS, F. VAN (1971). *J. Appl. Cryst.* **4**, 263-264.
- BROCK, C. P., KUO, M.-S. & LEVY, H. A. (1978). *Acta Cryst.* **B34**, 981-985.
- CAILLEAU, H. (1986). *Incommensurate Phases in Dielectrics*, Vol. 2, pp. 71-99. Amsterdam: North-Holland.
- CAILLEAU, H., BAUDOUR, J. L., MEINNEL, J., DWORKIN, A., MOUSSA, F. & ZEYEN, C. M. E. (1980). *Faraday Discuss. Chem. Soc.* **69**, 7-18.
- CAILLEAU, H., MESSEGER, J. C., MOUSSA, F., BUGAUT, F., ZEYEN, C. M. E. & VETTER, C. (1986). *Ferroelectrics*, **67**, 3-14.
- CHARBONNEAU, G. P. & DÉLUGEARD, Y. (1976). *Acta Cryst.* **B32**, 1420-1423.
- CHARBONNEAU, G. P. & DÉLUGEARD, Y. (1977). *Acta Cryst.* **B33**, 1586-1588.
- HALSTEAD, T. K., SPIESS, H. W. & HAEBERLEN, U. (1976). *Mol. Phys.* **31**(5), 1569-1583.
- HALSTEAD, T. K., TAGENFELDT, J. & HAEBERLEN, U. (1981). *J. Chem. Soc. Faraday Trans. 2*, **77**, 1817.
- HEINE, V. & PRICE, S. L. (1985). *J. Phys. C*, **18**, 5259-5278.
- JOHNSON, C. K. (1980). In *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN. Bangalore: Indian Academy of Sciences.
- KRONEBUSCH, P., GLEASON, W. B. & BRITTON, D. (1976). *Cryst. Struct. Commun.* **5**, 839-842.
- NATKANIEC, I., BIELUSHKIN, A. V. & WASIUTYNSKI, T. (1981). *Phys. Status Solidi B*, **105**, 413-423.
- PLAKIDA, N. M., BIELUSHKIN, A. V., NATKANIEC, I. & WASIUTYNSKI, T. (1983). *Phys. Status Solidi B*, **118**, 129-133.
- RAICH, J. C. & BERNSTEIN, E. R. (1984). *Mol. Phys.* **53**, 597-614.
- ROMMING, C. H. R., SEIP, H. M. & AANESSEN OYMO, I.-M. (1974). *Acta Chem. Scand. Ser. A*, **28**, 507-514.
- SAITO, K. (1986). Thesis, Osaka Univ., Japan.
- SAITO, K., ATAKE, T. & CHIHARA, H. (1986). *J. Chem. Thermodyn.* **18**, 407-414.
- SAITO, K., ATAKE, T. & CHIHARA, H. (1987). *Acta Cryst.* **B43**, 383-385.
- SAITO, K., CHIHARA, H., ATAKE, T. & SAITO, Y. (1985). *Jpn J. Appl. Phys.* **24**, 838-840.
- TAKEUCHI, H., SUZUKI, S., DIANOUX, A. J. & ALLEN, G. (1981). *Chem. Phys.* **55**, 153-162.
- TOUPET, L. & GIRARD, A. (1980). Private communication.
- WASIUTYNSKI, T., NATKANIEC, I. & BIELUSHKIN, A. V. (1981). *J. Phys. (Paris)*, **42**, C6-599.

Acta Cryst. (1987). **B43**, 470-479

Comparison Between Structural Analyses of Plastic and Brittle Crystals

BY J. P. AMOUREUX AND M. FOULON

Laboratoire de Dynamique des Cristaux Moléculaires (UA 801 CNRS), Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq CEDEX, France

(Received 15 April 1986; accepted 9 April 1987)

Abstract

The structures of adamantane (C₁₀H₁₆) and fluoroadamantane (C₁₀H₁₅F), in their plastic phases, are refined according to a Frenkel model or to the determination of the molecular orientational probability. A comparison is proposed between the A_{mm}^l coefficients refined in the second method and the librational amplitudes deduced from the Frenkel model. The experimental technique employed to obtain a good crystal in the low-temperature phase is described and the order-disorder transition process is discussed from the point of view of these structural studies. Crystal data for adamantane at 188 K: $M_r =$

136.3, tetragonal, $P\bar{4}_2c$, $a = 6.639(7)$, $c = 8.918(9)$ Å, $V = 393.1(12)$ Å³, $Z = 2$, $D_x = 1.15$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.064$ mm⁻¹, $F(000) = 152$, $R = 3.6\%$ for 211 independent reflections.

I. Introduction

Structural studies of disordered crystalline phases are commonly performed according to two different methods. In the first, the 'Frenkel model' describes the molecular disorder by discrete equilibrium positions and the thermal vibrations are split into librations and translations. In the second method, the

molecular orientational probability is decomposed into functions adapted to the molecular and lattice symmetries. The molecular orientations depend on the $A'_{mm'}$ coefficients of this decomposition which are the refined parameters.

The problem arises of how to compare the results obtained by these two methods. We have looked for a relation between the $A'_{mm'}$ coefficients and the librational amplitudes refined with the Frenkel model. This relation would allow us to introduce almost correct $A'_{mm'}$ values in the refinement according to the second method.

The proposed method is tested on two compounds of different molecular symmetries: adamantane ($C_{10}H_{16}$, T_d symmetry) and fluoroadamantane ($C_{10}H_{15}F$, C_{3v} symmetry) at two temperatures, 295 and about 226 K.

The structure of the ordered phase of adamantane has already been investigated at 163 K with X-ray precession photographs (Nordman & Schmitkons, 1965). However, with the 'poor and deteriorating quality of the diffraction patterns', only 53 independent reflections were evaluated and therefore the atomic positions and thermal parameters were not refined in an accurate way. It seemed interesting to obtain a good monocrystalline sample in this low-temperature phase in order to get better structural parameters and to have a better understanding of the order-disorder transition occurring in this compound.

II. General

Adamantane $C_{10}H_{16}$ is a spherical molecule of T_d symmetry which undergoes, below its melting point ($T_m = 541$ K), an order-disorder phase transition at $T_i = 208.6$ K (Clark, Knox, Mackle & Hervey, 1977). Fluoroadamantane $C_{10}H_{15}F$ is a globular molecule of C_{3v} symmetry obtained from adamantane by sub-

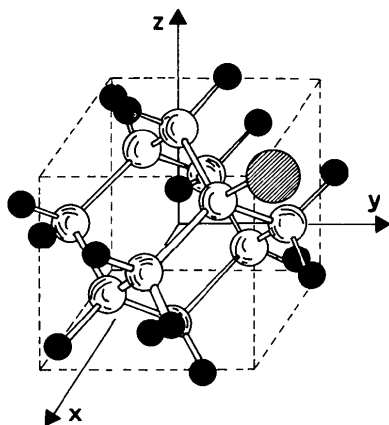


Fig. 1. The molecular structure of $C_{10}H_{15}F$. C atoms are white, H atoms are black and the F atom is shaded. The cube corresponds to the directions of the unit-cell edges in the plastic phase.

stituting an F atom for one methylene H atom (Fig. 1). Its melting and order-disorder transition temperatures are respectively $T_m = 525$ and $T_i = 221.6$ K.

Incoherent quasielastic neutron scattering (Bee, Amoureux & Lechner, 1980; Bee & Amoureux, 1983) has proved that these two compounds are in a rotator phase at room temperature. Preliminary structural analyses have shown that the mean space groups are both $Fm\bar{3}m$ with $Z = 4$ (Amoureux & Bee, 1980; Amoureux, Bee & Sauvajol, 1982). The four tertiary C atoms are always situated on the $\langle 111 \rangle$ directions and the six secondary C atoms on the $\langle 001 \rangle$ directions. This corresponds to two discernible equilibrium positions for $C_{10}H_{16}$ and to eight for $C_{10}H_{15}F$.

III. Data collection and weighting scheme

The data collections were performed on an automatic four-circle X-ray diffractometer (Philips PW 1100), with $Mo K\alpha$ radiation and a 0.8 mm \varnothing collimator. Crystals pyramidal, volumes 0.027–0.043 mm³. The intensities were measured, scanning the θ - 2θ range with approximate speeds and fixed widths of respectively 0.01° min⁻¹ and 1.4°. In order to be sure that no secondary extinction occurred, comparisons of strong reflections for several crystals were performed in the plastic phases. Within 5% the experimental intensities were always in the same ratio for all the crystals of each compound, and hence no extinction corrections were applied. The Bragg peaks of the low-temperature phase of $C_{10}H_{16}$ were recorded on a single crystal which was cooled down from room temperature. No extinction corrections were applied to the raw data obtained with this crystal which did not suffer from extinction in the plastic phase before cooling. As a result of the low absorption coefficients [μ , (cm⁻¹) = 0.64 for $C_{10}H_{16}$ and 0.88 for $C_{10}H_{15}F$], no corresponding corrections were applied.

In plastic crystals, some Bragg reflections (with low scattering vectors) have very strong intensities compared with the others and a weighting scheme must be introduced in order to use all the experimental data. The following weighted (wR) or unweighted (R) factors measure the quality of the refinement and have minimum values for the best fit:

$$wR^2 = \frac{\sum |F_o - |F_c||^2 \sigma^{-2}}{\sum F_o^2 \sigma^{-2}} \quad (1)$$

$$R = \frac{\sum |F_o - |F_c||}{\sum F_o}$$

with $\sigma^2 = \sigma_c^2 + E^2 F_o^2$. σ_c is the counting standard deviation and E is a constant value chosen so that R and wR become nearly equal. According to this condition, the best E values were 0 (295 K) and 0.003 (223 K) for $C_{10}H_{16}$ and 0.02 (295 K) and 0.01 (229 K) for $C_{10}H_{15}F$.

Table 1. *Crystal data for adamantane, T = 188 K*

Tetragonal,	Space group $P\bar{4}2_1c$,	$Z = 2$
$a = 6.639$ (7),	$c = 8.918$ (9) Å,	$V = 393.1$ (1.2) Å ³
$F(000) = 152$,	211 reflections with $I \geq 3\sigma(I)$	

The choice of the weighting scheme for the analysis of the low-temperature phase of $C_{10}H_{16}$ is much less important than for the plastic phase and the results remain nearly independent of the weighting law. The E value was 0.028 and 0.0 for the data collection at 188 K corresponding to the refinements with the *SHELX76* (Sheldrick, 1976) and *ORION* (André, Fourme & Renaud, 1971) programs respectively [see § IV.(3)].

IV. Low-temperature phase of adamantane

(1) Experiment

The growth of the single crystal at low temperature ($T < T_i = 208.6$ K) and its setting on the diffractometer, successfully used in the case of chloroadamantane ($T_i = 246$ K) (Foulon, 1986), failed because the temperature of the phase transition is too low. A continuous slow cooling of samples randomly set in gaseous nitrogen flow leads to the breaking of the crystal into several domains.

A better method was to orientate one fourfold cubic axis parallel to the nitrogen flow direction, in the plastic phase. The temperature was decreased slowly to 209 K and kept constant for 2 h. Then the sample was cooled very slowly to 200 K in 1 h. The crystal passed into the low-temperature phase without much damage: the reflection widths (FWHM) were 0.25 and 0.34° respectively in the high- and low-temperature phases.

The same method was used in the case of fluoroadamantane, but unfortunately the numerous attempts always failed and the low-temperature phase of this compound is still unknown.

(2) Lattice parameters (Table 1)

The low-temperature phase of adamantane crystallizes in the tetragonal system with the $P\bar{4}2_1c$ space group in agreement with the previous determination (Nordman & Schmitkons, 1965). 25 reflections were used to determine lattice parameters, $\sin \theta / \lambda \leq 0.30 \text{ \AA}^{-1}$.

In order to characterize the lattice modifications at the phase transition, a 'pseudo'-cubic cell (\mathbf{a}' , \mathbf{b}' , \mathbf{c}') may be built on the tetragonal one (\mathbf{a}_T , \mathbf{b}_T , \mathbf{c}_T). This leads to the well known transformation

$$\begin{aligned} \mathbf{a}' &= \mathbf{a}_T + \mathbf{b}_T \\ \mathbf{b}' &= \mathbf{b}_T - \mathbf{a}_T \\ \mathbf{c}' &= \mathbf{c}_T. \end{aligned} \quad (2)$$

The variations of the lattice parameters of the pseudo (c_T , $a' = b' = a_T 2^{1/2}$) and plastic (a_c) cubic phases are drawn in Fig. 2.

(a) The preserved fourfold axis (\mathbf{c}_T) undergoes an important decrease at the transition [$c_T/a_c = 0.960$ (2)], which may explain the difficulties in obtaining a good crystal on lowering the temperature. This \mathbf{c}_T direction was the one which was set parallel to the nitrogen flow (in the above-mentioned method) which consequently favours this oriented domain over a very weak temperature gradient parallel to the gas flow. The temperature variation of c_T follows a linear law with about the same dilatation coefficient as in the plastic phase:

$$\alpha(c_T) = 1.36 \times 10^{-4} \text{ K}^{-1}, \quad \alpha(a_c) = 1.21 \times 10^{-4} \text{ K}^{-1}.$$

(b) On the other hand, the two other fourfold axes (in the plastic phase) remain nearly constant at the transition: $a_T 2^{1/2}/a_c = 1.006$ (2). In the tetragonal phase the linear variation of a_T is about three times smaller than that of c_T : $\alpha(a_T) = 0.42 \times 10^{-4} \text{ K}^{-1}$. It is foreseeable that the phase transition will have little influence on the molecular arrangement in the (\mathbf{a}_T , \mathbf{b}_T) plane, but will change it along the \mathbf{c}_T axis.

(c) The ratio $c_T/a_T 2^{1/2}$, which measures the deviation with respect to the cubic cell, increases with temperature. Its value of 0.95 at 208 K is comparable with that of cyanoadamantane at its transition: 0.93 (Foulon, Amoureux, Sauvajol, Cavrot & Muller, 1984).

(d) Fig. 3 shows the variation of the calculated cell volume for the plastic (V_c) and low-temperature phases ($V' = 2V_T$). The important gap at the transition

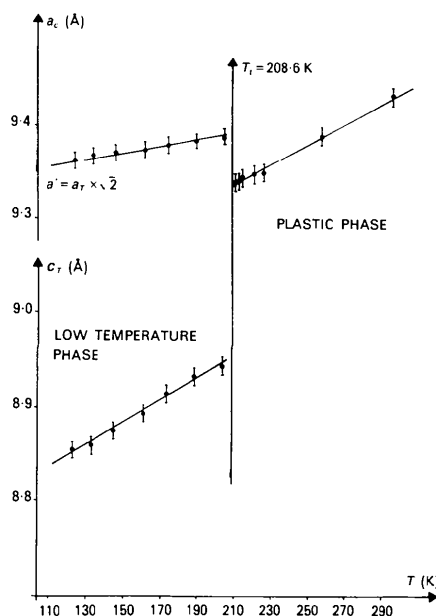


Fig. 2. Variations of the lattice parameters of the pseudo (c_T , $a' = b' = a_T 2^{1/2}$) and plastic (a_c) cubic phases.

[$V_c/V' = 1.030(6)$] and the significant difference between the slopes ($\alpha_{V_c}/\alpha_{V'} = 1.73$) are certainly related to the modification of the dynamical disorder.

The volume occupied by a 'static' adamantane molecule, according to a model in which the atoms are represented as spheres with van der Waals radii, is $V_s = 145 \text{ \AA}^3$. At the transition, the compactness factors are then $\varepsilon_c^s = 0.714$ and $\varepsilon_T^s = 0.735$. These values may be compared with the close packing of spheres in the cut-sphere approximation: $\varepsilon = 0.74$. From this point of view, it can be expected that the low-temperature phase of adamantane still presents some slow dynamical disorder.

In the plastic phase, it is well known (Amoureux & Bee, 1980) that the molecule can occupy two discernible positions leading to fast endospherical rotations (Bee, Amoureux & Lechner, 1980). In order to take into account this dynamical disorder and to get an overestimation of the volume occupied by a molecule at each site, the volume of a fictitious 'dynamical' (D) molecule was calculated, assuming that the two positions coexist: $V_D = 165 \text{ \AA}^3$. This corresponds to too high a compactness factor $\varepsilon_c^D = 0.813$, which proves that all molecules cannot rotate freely independently of the neighbourhood.

(3) Crystallographic results (Table 2)

365 unique Bragg reflections were measured at 188 K and 211 independent ones [$I \geq 3\sigma(I)$] introduced in the refinements. $\sin \theta/\lambda \leq 0.070 \text{ \AA}^{-1}$; $0 \leq h, k \leq 9, 0 \leq l \leq 12$. 25 reflections were used for lattice-parameter determination with $\sin \theta/\lambda \leq 0.30 \text{ \AA}^{-1}$. The intensities of 3 standard reflections ($\bar{2}02$, $0\bar{2}\bar{2}$ and

201) varied by +1%. The refinements were based on F . The H atoms were introduced at calculated positions and their atomic positions were refined. Maximum shift/e.s.d. ~ 0.005 . Maximum and minimum peak heights in the final difference Fourier synthesis were 0.18 and -0.23 e \AA^{-3} . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). A CII Honeywell Bull MIMI6 computer was used for all calculations.

The refinements were performed in two ways, starting from the known structure (Nordman & Schmitkons, 1965). At first the atoms were considered independent. The thermal parameters introduced as the usual U_{ij} parameters were constrained according to the atomic site symmetry with the *SHELX* program (Sheldrick, 1976). The second procedure assumes that the adamantane molecule is a rigid group: *ORION* program (André, Fourme & Renaud, 1971). In this model, the thermal vibrations are described by the classical **T**, **L**, **S** tensors. According to the site symmetry only six non-vanishing coefficients are to be refined and their final values are reported in Table 2.*

These two refinement methods lead to very similar results, which proves that this molecule can be considered as a rigid group. The intramolecular bond distances and angles are in good agreement with those found in the literature (Table 2). The molecular mass centres occupy the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites of the tetragonal lattice corresponding to the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ f.c.c. ones. One $\bar{4}$ molecular axis remains located on the $\langle 001 \rangle$ fourfold lattice axis. The two other $\bar{4}$ molecular axes, originally elongated along the $\langle 100 \rangle$ and $\langle 010 \rangle$ cubic directions in the plastic phase, undergo an 8° rotation about the $\langle 001 \rangle$ axis in the low-temperature phase. Each of the two molecules in the unit cell can be obtained from the other by a 74° rotation about $\langle 001 \rangle$. Fig. 4 shows a projection of the structure along the $\langle 001 \rangle$ directions. The atoms of the molecules are drawn as spheres of van der Waals radii. The molecular packing in the (001) planes is practically identical to that of the plastic phase, but the contraction of these planes leads to the 8° rotation of the molecules mentioned above. Nevertheless, the study of the steric hindrance shows that the intermolecular contacts are weak. The distances, interpolated at 208 K, between the molecular mass centre at $(0, 0, 0)$ and its first and second neighbours are respectively 6.60 and 9.33 \AA in the plastic phase and 6.64 , 6.49 , 8.95 and 9.39 \AA in the tetragonal phase.

The analysis of the thermal vibrations in terms of the **T**, **L**, **S** tensors (Table 2) leads to quasi-isotropic translations: [$T_i = 0.019(1) \text{ \AA}^2$]. In the plastic phase,

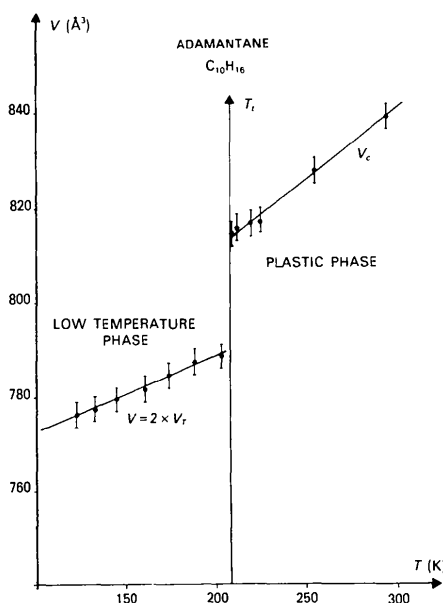


Fig. 3. Variation of the calculated cell volume for the plastic (V_c) and low-temperature phases ($V' = 2V_T$).

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43883 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Crystallographic results

	Independent atoms (<i>SHELX</i>)			$U_{11}(U_{iso}) (\text{Å}^2)$	$U_{22} (\text{Å}^2)$	$U_{33} (\text{Å}^2)$	$U_{12} (\text{Å}^2)$	$U_{13} (\text{Å}^2)$	$U_{23} (\text{Å}^2)$
	<i>x</i>	<i>y</i>	<i>z</i>						
C(1)	0	0	0.1980 (3)	0.0357 (20)	0.0319 (19)	0.0219 (12)	-0.0009 (23)	0	0
C(2)	-0.0262 (4)	0.1862 (4)	0.0992 (3)	0.0317 (12)	0.0199 (10)	0.0287 (10)	0.0008 (10)	0.0021 (12)	-0.0063 (10)
C(3)	0.1600 (4)	0.2122 (4)	0	0.0271 (11)	0.0260 (10)	0.0385 (12)	-0.0078 (8)	0.0003 (14)	0.0001 (14)
HC(1)	0.1156 (40)	0.0099 (73)	0.2688 (27)	0.0428 (40)					
HC(2)	-0.0355 (50)	0.3016 (46)	0.1590 (32)	0.0428 (40)					
HC(3)	0.2817 (53)	0.2303 (48)	0.0626 (33)	0.0428 (40)					
H'C(3)	0.1427 (48)	0.3286 (47)	-0.0570 (33)	0.0428 (40)					

$$\langle d(C-C) \rangle = 1.529 (3) \text{ Å} \quad \langle \angle C-C-C \rangle = 109.5 (4)^\circ$$

$$R = 3.6, wR = 3.9\%$$

Rigid group (*ORION*) [$w^2 = 1/\sigma_c^2(F)$]

$$T_{11} = T_{22} = 0.0183 (12), T_{33} = 0.0211 (12) \text{ Å}^2$$

$$L_{11}^{1/2} = L_{22}^{1/2} = 4.3 (5), L_{33}^{1/2} = 3.7 (5)^\circ$$

$$S_{11} - S_{22} = -2(S_{22} - S_{33}) = -2(S_{33} - S_{11}) = 0.00106 (101),$$

$$S_{12} = S_{21} = -0.00002 (71)$$

$$R = 4.0, wR = 2.4\%.$$

Table 3. Results with the Frenkel model

NT is the number of observed ($F_o/\sigma \geq 3$) independent Bragg peaks.										
	<i>T</i> (K)	w <i>R</i> (%)	<i>R</i> (%)	$T_i (\text{Å}^2)$	$T_{11} (\text{Å}^2)$	$T_{33} (\text{Å}^2)$	$L_i^{1/2} (^\circ)$	$L_{\perp}^{1/2} (^\circ)$	$L_{\parallel}^{1/2} (^\circ)$	NT
$C_{10}H_{16}$	223	4.9	4.9	0.037 (2)			7.8 (2)			79
	295	8.0	7.7	0.049 (2)			9.2 (2)			66
	188	2.4	4.0	0.019 (1)			4.1 (5)			211
$C_{10}H_{15}F$	229	7.9	10.1	0.038 (3)			6.5 (2)			98
		7.3	8.9	0.038 (3)				5.6 (3)	8.8 (6)	
		7.1	8.8		0.045 (6)	0.028 (8)		5.5 (3)	8.8 (6)	
	295	7.2	5.0	0.061 (2)			8.1 (2)			52
		6.2	4.5	0.060 (2)				6.8 (3)	11.1 (7)	
	6.0	4.4		0.070 (6)	0.048 (9)		6.8 (3)	10.7 (7)		

this term follows a linear temperature variation (Table 3), whose interpolated value at 188 K [$T_i = 0.031 (2) \text{ Å}^2$] is much larger than the preceding one in the low-temperature phase. The difference (0.012 Å^2) probably arises from a local deformation of the cubic lattice which corresponds to a static disorder (Meyer & Ciccotti, 1985).

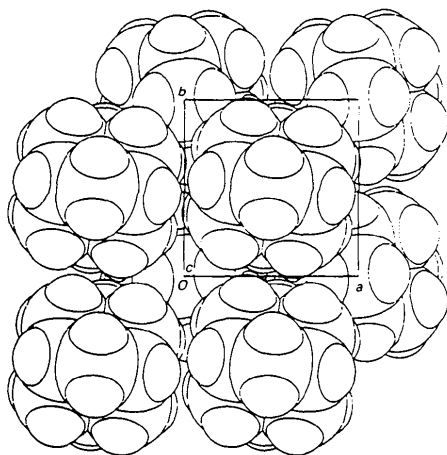


Fig. 4. Projection of the structure along the (001) direction.

The *L* tensor is also quasi-isotropic in the ordered phase with $L_i^{1/2} = 4.1 (5)^\circ$. This value is relatively high compared with usual ordered crystals at this temperature. This may be significant of some quasi-isotropic molecular motion. However, the L_i value increases largely at the transition which may correspond to the important acceleration of the molecular reorientations. The null S_{ij} coefficients (within the error bars) show that the translation-rotation coupling is negligible. The analysis of the residual electronic density reveals no disorder and consequently the molecules occupy only one equilibrium position at each site, unlike the two discernible positions in the plastic phase.

All these crystallographic discussions corroborate the NMR studies (Resing, 1969), which show that, in its two solid phases, the adamantane molecules carry out an endospherical motion characterized by the following residence times:

$$\text{cubic: } \tau_c(s) = 9.4 \times 10^{-14} \exp(1549/T)$$

$$\text{tetragonal: } \tau_T(s) = 1.13 \times 10^{-15} \exp(3268/T).$$

In the low-temperature phase, the reorientational process is largely slackened ($\tau_T/\tau_c = 47$ at T_i) and the activation energy is doubled.

V. Structural methods used in plastic phases

For adamantane (fluoroadamantane), reflections were collected for $0 \leq h \leq 14$ ($0 \leq h \leq 16$) with $\sin \theta/\lambda \leq 0.75 \text{ \AA}^{-1}$ ($\sin \theta/\lambda \leq 0.96 \text{ \AA}^{-1}$). Intensities of 3 standard reflections (311, 422 and 333) varied by $\pm 1\%$. 86 (98) unique reflections were measured with $R_{\text{int}} \leq 1\%$.

The two molecules ($C_{10}H_{16}$ and $C_{10}H_{15}F$) are considered rigid. The molecular distances and angles have been fixed (within 1%) at their values refined in the low-temperature phase, assuming that the F atom does not change the geometry of the adamantyl group ($C-F = 1.38 \text{ \AA}$). Structural analyses of plastic crystals can be carried out either with a Frenkel model or with a decomposition of the atomic orientational probability on symmetry-adapted functions.

(1) Frenkel model

The atoms are fixed on well defined equilibrium positions: their orientational probabilities are Dirac δ functions. In a harmonic approximation the thermal motions are described by three tensors: **T** (translations), **L** (librations) and **S** (translation-rotation coupling).

The two symmetrical **T** and **L** tensors must take into account the molecular symmetry and the local order created by the neighbouring molecules. We have assumed that, in these two compounds, the time-averaged local order (for a particular equilibrium position) has at least the same symmetry as the molecule. This assumption concerns exclusively the relative orientations of nearest-neighbour molecules as their mass centres follow the cubic point-group symmetry.

In the case of fluoroadamantane, the C_{3v} molecular symmetry introduces *a priori* four mean-square amplitudes representing:

- L_{\parallel} : the librations around the molecular threefold axis Δ ;
- L_{\perp} : the librations around any axis perpendicular to Δ ;
- T_{\parallel} : the translations along Δ ;
- T_{\perp} : the translations in the plane perpendicular to Δ .

When thermal motions can be considered as isotropic (as for $C_{10}H_{16}$: T_d symmetry), only two parameters subsist: $T_{\parallel} = T_{\perp}$ and $L_{\parallel} = L_{\perp}$. In the 'linear' approximation of Willis & Pawley (1969), these thermal motions have two simple analytical effects on the structure factors:

(a) They correspond to a classical Debye-Waller factor e^{-W} :

$$W/2\pi^2 = X_{\parallel}^2 T_{\parallel} + X_{\perp}^2 T_{\perp} + (\mathbf{X} \wedge \mathbf{R})_{\parallel}^2 L_{\parallel} + (\mathbf{X} \wedge \mathbf{R})_{\perp}^2 L_{\perp}. \quad (3)$$

\mathbf{X} is the scattering vector and \mathbf{R} the vector joining each atom to the molecular mass centre. X_{\parallel} , $(\mathbf{X} \wedge \mathbf{R})_{\parallel}$, X_{\perp} and $(\mathbf{X} \wedge \mathbf{R})_{\perp}$ are the components of \mathbf{X} and $\mathbf{X} \wedge \mathbf{R}$ respectively along and perpendicular to Δ .

(b) They introduce an 'artificial' shortening effect ($\Delta R/R$) which is equal to L_i (rad^2) for isotropic librations.

The preceding tensorial harmonic description is only available for small thermal motions. Hohlwein (1984) has computed the librational effects on diffracted intensities accurately and shown that for small amplitudes ($L^{1/2} \leq 10^\circ$) the formulae of Willis & Pawley give a fine description, which will be used in the following.

If we only take into account the molecular symmetries, the **S** tensor vanishes in $C_{10}H_{16}$ (T_d) and has a single independent element ($S_{12} = -S_{21}$) in the molecular referential of $C_{10}H_{15}F$ (C_{3v}). The librational amplitudes are small in the latter compound and then its S_{12} term can be neglected as was verified in the refinements.

(2) Analysis with symmetry-adapted functions

This method has been described in a preceding paper (Amoureux, Sauvajol & Bee, 1981) and we shall only recall its main results. If we neglect the translation-rotation coupling, the structure factor can be written as a product of two terms:

$$F(\mathbf{X}) = \exp(-2\pi^2 \mathbf{X}^2 T_i) \sum_{l,m,m'} i^l A_{mm'}^l T_m^l(\mathbf{X}) K_m^l(\mathbf{X}). \quad (4)$$

The first term corresponds to the translations and in this method it has isotropic Debye-Waller lattice symmetry.

In the second rotational term, the lattice symmetry is represented by the classical cubic harmonics K_m^l and the molecular symmetry influences the T_m^l terms by means of $M_m^l(\Omega_M^\mu)$:

$$T_m^l(\mathbf{X}) = 4\pi \sum_{\mu} j_l(2\pi \mathbf{X} R_{\mu}) M_m^l(\Omega_M^\mu) n_{\mu} f_{\mu}(X). \quad (5)$$

$f_{\mu}(X)$ and R_{μ} are the atomic scattering factor and the distance to the averaged molecular mass centre of the n_{μ} equivalent atoms of the μ th shell. j_l is the spherical Bessel function of order l .

The $M_m^l(\Omega_M^\mu)$ terms correspond to the values of the molecular symmetry-adapted functions M_m^l for the polar angles Ω_M^μ describing the atom μ in the molecular frame.

The time-averaged orientation of the molecule in the cubic lattice is fixed by the $A_{mm'}^l$ refined parameters. We have already shown that in their plastic phases the space group of these two compounds is $Fm\bar{3}m$. Therefore the only non-zero $A_{mm'}^l$ terms correspond to l even with $A_{11}^0 = 1$ and $A_{mm'}^2 = 0$.

The orientational averaged probability density of atoms of the μ th shell, with respect to the cubic

lattice, can be written as a linear development of cubic harmonics:

$$\vartheta_{\mu}^{\text{CH}}(\Omega) = \sum_{l,m,m'} A_{lmm'}^l M_{m'}^l(\Omega_M^{\mu}) K_m^l(\Omega). \quad (6)$$

The free isotropic rotation corresponds to the zeroth order only [$\vartheta_{\mu}^{\text{CH}}(\Omega) = 1/4\pi$]. The more localized the molecular orientations, the higher the l order needed in the refinements. In the following, for clarity, we shall write $A_{lmm'}^l$ in the general case, $\hat{A}_{lmm'}^l$ when the molecular symmetry is T_d and $\hat{A}_{lmm'}^l$ when it is C_{3v} .

(a) *Adamantane*. The functions adapted to the molecular (T_d) and lattice (O_h) symmetries are identical [$M_{m'}^l(\Omega) = K_m^l(\Omega)$] and there exist only four parameters up to order 10 (\hat{A}_{111}^1) and four more of order 12, \hat{A}_{111}^{12} , ($m, m' = 1$ or 2).

(b) *Fluoroadamantane*. The functions adapted to this C_{3v} molecular symmetry correspond for the Δ dipolar axis to $M_{m'}^l(\Delta) = [(2l+1)/4\pi]^{1/2} \delta_{1,m'}$. Therefore, the orientation of the Δ axis depends only on the \hat{A}_{m1}^l terms (6):

$$\vartheta_{\Delta}^{\text{CH}}(\Omega) = \sum_{l,m} \hat{A}_{m1}^l [(2l+1)/4\pi]^{1/2} K_m^l(\Omega). \quad (7)$$

The remaining $\hat{A}_{lmm'}^l$ ones ($m' \neq 1$) determine the molecular orientation around this Δ dipolar axis. These terms are all equal to zero for a constant cylindrical charge density around this Δ axis.

In the general case, there are too many parameters to be refined (24 up to order 12) with respect to the number of observed independent Bragg reflections. We have then to set aside those which have a small influence on the structure factors. These unrefinable $\hat{A}_{lmm'}^l$ terms correspond to $T_{m'}^l$ values nearly negligible for this particular molecule.

(3) Comparison between the two methods

The orientational probability with respect to the cubic lattice of the atoms μ can be defined in two ways: $\vartheta_{\mu}^{\text{CH}}(\Omega)$ (6) with cubic harmonics; and $\vartheta_{\mu}^{\text{FR}}(\Omega)$ with the Frenkel model. In the second model the librations are assumed harmonic and then $\vartheta_{\mu}^{\text{FR}}(\Omega)$ is composed of N Gaussian functions corresponding to the N 'equilibrium positions' of atoms μ . In the following we shall compare these two functions only for atoms whose librations can be assumed isotropic in the Frenkel model. These atoms are all those of adamantane (L_i) and those situated on the dipolar axis in fluoroadamantane (L_{\perp}).

The comparison between ϑ^{CH} and ϑ^{FR} is very difficult for atoms of $C_{10}H_{15}F$ outside this Δ axis because the Gaussian functions are then anisotropic and the integrations of equations (A8) and (A9) much more complicated.

(a) *Global comparison*. If we compare the maximum values corresponding to the 'equilibrium

positions', one gets a global relation between the $A_{lmm'}^l$ and the librational amplitude of these compounds.

In adamantane there exist *a priori* three 'independent' shells ($\Omega_M^{\mu} \neq \Omega_{M'}^{\mu}$) (Prandl, 1981) corresponding to the secondary (Cs) and tertiary (Ct) C atoms and to the secondary H atoms. However, in X-ray diffraction, only the C atoms are important and will be considered in the following. According to their N equilibrium positions, the maximum orientational probabilities of atoms with isotropic librations are [(6) and (7)]

$$\vartheta_{C_{s,\max}}^{\text{CH}} = \sum_{lmm'} \hat{A}_{lmm'}^l K_m^l(001) K_{m'}^l(001) \quad (8)$$

$$\vartheta_{C_{t,\max}}^{\text{CH}} = \sum_{lmm'} \hat{A}_{lmm'}^l K_m^l(111) K_{m'}^l(111) \quad (9)$$

$$\vartheta_{\Delta,\max}^{\text{CH}} = \sum_{l,m} \hat{A}_{m1}^l [(2l+1)/4\pi]^{1/2} K_m^l(111) \quad (10)$$

and

$$\vartheta_{\mu,\max}^{\text{FR}} = (2\pi NL)^{-1}. \quad (11)$$

N is equal to 6 (Ct) or 8 (Δ and Cs) and L to L_i (Ct and Cs) or L_{\perp} (Δ).

(b) *Detailed comparison*. It is also possible to decompose $\vartheta^{\text{FR}}(\Omega)$ on the cubic harmonics $K_m^l(\Omega)$ by assuming that this orientational probability has exactly the same symmetry as $\vartheta^{\text{CH}}(\Omega)$ (Appendix). This is only an approximation because these two functions respect the cubic symmetry, but the libra-

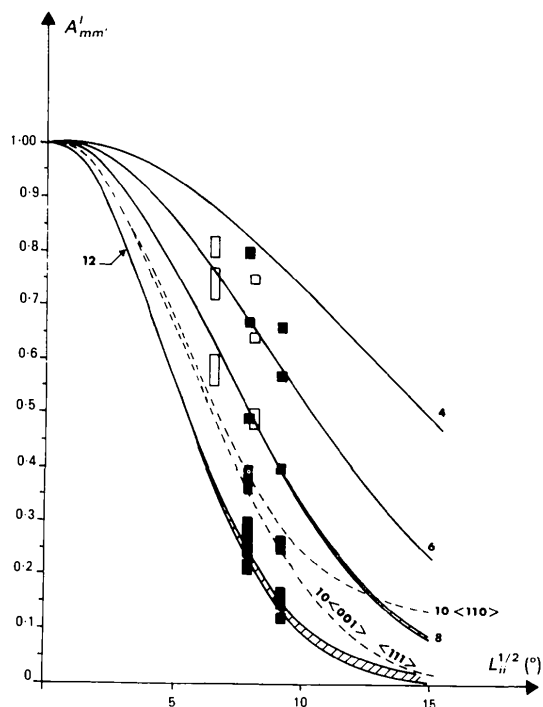


Fig. 5. Relative evolution of $A^l/A^l(f)$ with respect to the isotropic librational amplitude $L^{1/2}$ ($^{\circ}$): \blacksquare $C_{10}H_{16}$ (223 and 295 K); \square $C_{10}H_{15}F$ (229 and 295 K).

Table 4. Results with the cubic harmonics K_m^l as symmetry-adapted functions

For fluoradamantane a pseudo $C_{10}H_{15}F$ molecule with T_d symmetry has been used.											
	T (K)	wR (%)	R (%)	T_i (\AA^2)	\hat{A}_{11}^4	\hat{A}_{11}^6	\hat{A}_{11}^8	\hat{A}_{11}^{10}	\hat{A}_{11}^{12}	\hat{A}_{22}^{12}	\hat{A}_{12}^{12}
$C_{10}H_{16}$	223	3.9	4.9	0.034 (2)	0.80 (1)	0.67 (1)	0.49 (1)	0.37 (3)	0.24 (4)	0.27 (4)	
	295	1.4	1.8	0.047 (1)	0.66 (1)	0.57 (1)	0.40 (1)	0.26 (2)	0.12 (1)	0.16 (2)	-0.43 (3)
$C_{10}H_{15}F$	229	12	11	0.038 (3)	0.81 (2)	0.74 (3)	0.58 (3)	0.37 (11)	0.30 (9)	0.18 (18)	
	295	4.9	4.8	0.062 (2)	0.75 (1)	0.64 (1)	0.49 (2)	0.51 (3)	0.30 (3)	0.43 (5)	

Table 5. Results for $C_{10}H_{15}F$ with C_{3v} symmetry

T (K)	wR (%)	R (%)	T_i (\AA^2)	\hat{A}_{11}^4	\hat{A}_{12}^4	\hat{A}_{11}^6	\hat{A}_{13}^6	\hat{A}_{11}^8
Molecule fixed: $\hat{A}_{mm}^l(f)$				-0.51	0.86	0.63	0.56	0.21
229	6.7	6.9	0.041 (2)	-0.44 (4)	0.78 (4)	0.50 (5)	0.52 (6)	0.15 (3)
	$\hat{A}_{m1}^l/\hat{A}_{m1}^l(f)$			0.86 (8)		0.79 (8)		0.71 (14)
295	4.2	3.1	0.060 (2)	-0.34 (3)	0.64 (3)	0.43 (4)	0.48 (3)	0.11 (3)
	$\hat{A}_{m1}^l/\hat{A}_{m1}^l(f)$			0.67 (6)		0.68 (6)		0.52 (14)
T (K)	wR (%)	R (%)	\hat{A}_{13}^8	\hat{A}_{11}^{10}	\hat{A}_{14}^{10}	\hat{A}_{13}^{12}	\hat{A}_{15}^{12}	\hat{A}_{21}^{12}
Molecule fixed: $\hat{A}_{mm}^l(f)$				0.75	-0.65	0.60	-0.53	0.07
229	6.7	6.9	0.071 (3)	-0.38 (5)	0.58 (18)	-0.45 (14)	0.98 (25)	-0.23 (5)
	$\hat{A}_{m1}^l/\hat{A}_{m1}^l(f)$			0.58 (8)				0.56 (12)
295	4.2	3.1	0.55 (2)	-0.30 (4)	0.54 (16)	-0.40 (8)	0.68 (16)	-0.20 (3)
	$\hat{A}_{m1}^l/\hat{A}_{m1}^l(f)$			0.46 (6)				0.48 (7)

tions have been assumed isotropic, for the considered atoms, only with the Frenkel model. In that case one obtains a relation (Fig. 5) between each \hat{A}_{mm}^l and L_i for $C_{10}H_{16}$ and between each \hat{A}_{m1}^l and L_{\perp} for $C_{10}H_{15}F$.

VI. Results in the plastic phase

(1) Adamantane (Tables 3 and 4)

If we take into account the error bars, the isotropic translational amplitudes T_i are always identical in the two methods.

As was foreseeable, contrary to the Frenkel model, the method with symmetry-adapted functions is more suitable when the molecular orientations are less localized at high temperature. When the temperature decreases, the \hat{A}_{mm}^l terms tend to δ_{mm} , which corresponds to the molecules fixed without any librations.

The maximum values of the orientational probability are quasi-identical in these two methods: Table 6.

The \hat{A}_{mm}^l parameters refined directly with the symmetry-adapted functions are in good agreement with the corresponding ones deduced from the L_i value refined with the Frenkel model (Fig. 5). Only \hat{A}_{11}^4 is lower than its calculated value especially at 295 K.

(2) Fluoradamantane (Tables 3 and 5)

At 229 K, in the description with symmetry-adapted functions, only 62 Bragg peaks, so that $X \leq 1.3 \text{\AA}^{-1}$ ($h^2 + k^2 + l^2 \leq 150$), were introduced in the refinements. Indeed, the 36 other reflections correspond to so large an X value that the spherical Bessel

Table 6. $\vartheta_{\mu, \max}$ values deduced from the Frenkel model and the cubic harmonic description

Atom μ	$C_{10}H_{16}$		$C_{10}H_{15}F$			
	C_t	C_s	Δ			
T (K)	223	295	223	295	229	295
FR	1.05 (6)	0.76 (3)	1.39 (7)	1.02 (4)	2.16 (19)	1.39 (11)
CH	0.93 (4)	0.72 (3)	1.27 (6)	0.90 (3)	1.21 (15)	1.00 (11)

functions $j_l(2\pi X R_{C_s})$ of (5) become important only for $l \geq 14$. Therefore, the use of these 36 reflections would have needed a lot of extra \hat{A}_{mm}^l parameters ($l \geq 14$). The two different methods always give the same isotropic translational amplitudes T_i . Introduction of anisotropic translations in the refinements ($T_{\parallel} \neq T_{\perp}$) is not really conclusive: the R factor only decreases by 0.1%. At the two temperatures the librational amplitudes are small for a plastic crystal and then the Frenkel model gives a good description of reality with only four parameters. The method with symmetry-adapted functions also gives fine results, but requires a lot of \hat{A}_{mm}^l parameters and is only interesting at high temperature when the librational amplitudes are important.

The maximum values of $\vartheta(\Delta)$ deduced from the two methods are not in agreement particularly at 229 K when the Δ axis is very localized ($L_{\perp}^{1/2} = 5.6^\circ$). We have just seen that a correct description of fluoradamantane would have needed the use of high l in the refinements ($l \geq 14$). This lack of extra \hat{A}_{mm}^l terms ($l \geq 14$) corresponds to the differences in the $\vartheta(\Delta)$ values (Table 6). When the temperature

decreases (Table 5), all the refined $\hat{A}_{mm'}^i$ terms (except \hat{A}_{15}^{i2}) tend to their value corresponding to the molecule fixed without any librations: $\hat{A}_{mm'}^i(f)$. The relative refined values $\hat{A}_{m1}^i/\hat{A}_{m1}^i(f)$ are in reasonable agreement with the corresponding ones deduced from the L_{\perp} Frenkel value.

The only disagreement between these refined and calculated terms is \hat{A}_{11}^4 at 295 K (-0.34 instead of -0.42). However, as mentioned before, we could not refine all the $\hat{A}_{mm'}^i$ terms up to order 12. According to the parameters introduced in the refinements, the \hat{A}_{m1}^i values vary slightly. The comparison between refined and calculated \hat{A}_{m1}^i is then less easy than with a molecule of T_d symmetry. Moreover, as there are a lot of refined parameters, the e.s.d. of the \hat{A}_{m1}^i is important.

(3) $C_{10}H_{15}F$: approximation with pseudo T_d molecular symmetry (Table 4)

From the electronic point of view, the $C_{10}H_{16}$ and $C_{10}H_{15}F$ molecules are very close, as they differ only by the substitution of one F atom for a methylene H atom. This substitution corresponds, for the electronic charges, to a 10% change in amplitude and to a small displacement from the molecular mass centre: 2.6 to 2.9 Å.

We have replaced the three tertiary H atoms and the F atom by four 'pseudo' identical atoms, situated 2.83 Å from the averaged molecular mass centre, each of them composed of 0.75 H and 0.25 F atoms. This 'pseudo' molecule of T_d symmetry has the same global electronic charge as the $C_{10}H_{15}F$ molecule and is close to it. This approximation allows us to use the cubic harmonics as symmetry-adapted functions, which introduces a small number of $\hat{A}_{mm'}^i$ parameters in the refinements. This approximation is mainly available (small R value) at high temperature when the librational amplitude is important (Table 4).

The parameters of order 10 or 12 have no accurate value because of the approximations made in this method. As T_d molecular symmetry is used, one has to compare the results with those of the isotropic Frenkel model. If we consider only the refined \hat{A}_{11}^i parameters up to order 8, they are in agreement with the corresponding ones deduced from the L_i Frenkel value (Fig. 5).

VII. Concluding remarks

We have obtained detailed relations between the two usual structural analyses of plastic crystals: the Frenkel model and the decomposition of orientational probability on symmetry-adapted functions. These relations have been verified at two temperatures, on two plastic crystals of different molecular symmetries: adamantane (T_d) and fluoroadamantane (C_{3v}).

The Frenkel model needs only a very small number of parameters with very simple significances. Its description of the reality is all the better as the molecular orientations are localized: the thermal motions are assumed harmonic.

On the other hand, the method with symmetry-adapted functions always requires more parameters. Its use is mainly of interest when the molecular orientations are not localized and when the molecular symmetries are T_d or O_h .

We have also obtained a good single crystal of adamantane in its low-temperature phase, which has given a detailed description of the order-disorder transition in this compound.

APPENDIX

I. General formulation

Let us call Ω_M^{μ} and Ω_L^{μ} the polar angles describing the atom μ respectively in the molecular and cubic lattice frames.

If the librations of the μ th atom are assumed isotropic in the two models, which means that $\vartheta_{\mu}^{CH}(\Omega)$ and $\vartheta_{\mu}^{FR}(\Omega)$ have exactly the same symmetry, they become identical:

$$\begin{aligned} \sum_{lmm'} A_{mm'}^l M_m^l(\Omega_M^{\mu}) K_m^l(\Omega) \\ = (1/2\pi NL) \sum_{j=1}^N \exp(-\theta_{\mu j}^2/2L). \end{aligned} \quad (A1)$$

N is the number of different 'equilibrium positions' for the μ th atom and $\theta_{\mu j}$ represents the librational angle of atom μ about its j th 'equilibrium position'. L (L_i for $C_{10}H_{16}$ or L_{\perp} for the Δ axis of $C_{10}H_{15}F$) is the mean-square amplitude of the isotropic librations.

By using the orthonormalization properties of the K_m^l functions, one obtains

$$\begin{aligned} \sum_{m'} A_{mm'}^l M_m^l(\Omega_M^{\mu}) \\ = (1/2\pi NL) \sum_{j=1}^N \int \exp(-\theta_{\mu j}^2/2L) K_m^l(\Omega) d\Omega. \end{aligned} \quad (A2)$$

The 'equilibrium positions' and the K_m^l functions follow cubic symmetry. Therefore, the integrations corresponding to the N 'equilibrium positions' are all equal and then the subscript j may be removed from (A2):

$$\begin{aligned} \sum_{m'} A_{mm'}^l M_m^l(\Omega_M^{\mu}) \\ = (1/2\pi L) \int \exp(-\theta_{\mu}^2/2L) K_m^l(\Omega) d\Omega. \end{aligned} \quad (A3)$$

II. Lack of librations

When the molecules do not librate, the μ th atom is fixed on Ω_L^{μ} . In this case the $A_{mm'}^i(f)$ (f for fixed)

can be expressed as

$$\sum_{m'} A_{mm'}^l(f) M_{m'}^l(\Omega_M^\mu) = K_m^l(\Omega_L^\mu). \quad (A4)$$

When the molecular symmetry is T_d or O_h , the symmetry-adapted functions are then the cubic harmonics K_m^l :

$$\sum_{m'} \hat{A}_{mm'}^l(f) K_{m'}^l(\Omega_M^\mu) = K_m^l(\Omega_L^\mu). \quad (A5)$$

If, moreover, the molecular 'equilibrium positions' in the cubic lattice are identical to that in the molecular frame ($\Omega_M^\mu = \Omega_L^\mu$), one obtains, as for the fixed adamantane molecule:

$$\hat{A}_{mm'}^l(f) = \delta_{mm'}. \quad (A6)$$

If we now consider the molecular threefold axis Δ in $C_{10}H_{15}F$, the only non-zero $M_{m'}^l(\Omega_M^\Delta)$ terms correspond to $m' = 1$:

$$\hat{A}_{m1}^l(f) = [4\pi/(2l+1)]^{1/2} K_m^l(\Omega_L^\Delta). \quad (A7)$$

III. Librating molecules

In the case of librating adamantane molecules, one obtains

$$\hat{A}_{mm}^l = [2\pi L_i K_m^l(\Omega_M^\mu)]^{-1} \times \int \exp(-\theta_\mu^2/2L_i) K_m^l(\Omega) d\Omega. \quad (A8)$$

The \hat{A}_{m1}^l terms describing the orientation of the Δ dipolar axis of $C_{10}H_{15}F$ follow the relation:

$$\hat{A}_{m1}^l = (2\pi L_\perp)^{-1} [4\pi/(2l+1)]^{1/2} \times \int \exp(-\theta_\Delta^2/2L_\perp) K_m^l(\Omega) d\Omega. \quad (A9)$$

In both cases, the $A^l/A^l(f)$ ratios are given by (A8) and therefore they only depend on the 'equilibrium

positions' in the cubic lattice of the atom μ of $C_{10}H_{16}$ or Δ axis of $C_{10}H_{15}F$. Equation (A8) has been computed for different L values according to the 'equilibrium positions' along $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. The results are nearly independent of the 'equilibrium positions' with the exception of order ten for which the values along $\langle 110 \rangle$ are slightly higher than those along $\langle 001 \rangle$ and $\langle 111 \rangle$.

References

- AMOUREUX, J. P. & BEE, M. (1980). *Acta Cryst.* B36, 2636-2642.
 AMOUREUX, J. P., BEE, M. & SAUVAJOL, J. L. (1982). *Acta Cryst.* B38, 1984-1989.
 AMOUREUX, J. P., SAUVAJOL, J. L. & BEE, M. (1981). *Acta Cryst.* A37, 97-104.
 ANDRÉ, D., FOURME, R. & RENAUD, K. (1971). *Acta Cryst.* B27, 2371-2380.
 BEE, M. & AMOUREUX, J. P. (1983). *Mol. Phys.* 50, 585-602.
 BEE, M., AMOUREUX, J. P. & LECHNER, R. E. (1980). *Mol. Phys.* 40, 617-641.
 CLARK, T., KNOX, MC. O., MACKLE, H. & HERVEY, A. MC. (1977). *J. Chem. Soc. Faraday Trans.* 73(8), 1224-1231.
 FOULON, M. (1986). Private communication.
 FOULON, M., AMOUREUX, J. P., SAUVAJOL, J. L., CAVROT, J. P. & MULLER, M. (1984). *J. Phys. C*, 17, 4213-4229.
 HOHLWEIN, D. (1984). *Z. Kristallogr.* 169, 237-247.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 MEYER, M. & CICCOTTI, G. (1985). *Mol. Phys.* 56, 1235-1248.
 NORDMAN, C. E. & SCHMITKONS, D. L. (1965). *Acta Cryst.* 18, 764-767.
 PRANDL, W. (1981). *Acta Cryst.* A37, 811-818.
 RESING, H. A. (1969). *Mol. Cryst.* 9, 101.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 WILLIS, B. T. M. & PAWLEY, G. S. (1969). *Acta Cryst.* A26, 254-262.