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Structure of succinonitrile in its plastic phase

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Abstract. The structure of succinonitrile in its orientationally disordered phase was re-examined through extended x-ray diffraction measurements. It was solved by using both the analytic procedures of symmetry-adapted functions and a Frenkel model assuming discrete orientations. A possible translation–rotation coupling was included in this latter case via an offset vector e . The study confirms that the nitrogen atoms are localised along the fourfold axis of the cubic cell but evidences a strong offset of the centre of mass for *gauche* conformations. It is shown that this can be explained by steric hindrance between some configurations of neighbouring molecules.

1. Introduction

It was shown previously that, at room temperature, succinonitrile $\text{N}\equiv\text{C}-(\text{CH}_2)_2-\text{C}\equiv\text{N}$ crystallises in the $\text{Im}\bar{3}m$ space group ($a = 6.341 \text{ \AA}$) with two molecules per unit cell [1]. NMR [2], dielectric relaxation [3], Rayleigh scattering [4] and incoherent neutron scattering experiments [5–7] evidenced dynamic orientational disorder of the molecules. This plastic phase is stable from 233 K to the melting point at $T = 331 \text{ K}$. From x-ray diffraction and Raman scattering, it was found [1, 8, 9] that there is thermodynamic equilibrium between three isomeric forms as shown in figure 1: the *trans* isomer (*t*, figure 1(*b*)) with C_{2h} symmetry (the $\text{C}\equiv\text{N}$ groups are in the symmetry plane of the molecule); the *gauche* isomers (g_1 and g_2 , figures 1(*a*) and 1(*c*)) with C_2 symmetry (g_1 and g_2 are obtained from the *t* isomer by a relative rotation around the central C—C bond of $\pm 2\pi/3$ of one of the $\text{C}\equiv\text{N}$ groups with respect to the other).

The proportion of the *t* isomer at room temperature is 23% and increases slightly as a function of temperature [9]. The main features of the previous structure analysis assuming orientational disorder of the molecules but fixed centres of mass are as follows (figure 2).

(i) The molecule can align its central C—C bond along the four threefold axes of the cell.

(ii) Each $\text{C}\equiv\text{N}$ group can occupy three equilibrium positions which are obtained by a rotation of $2\pi/3$ around the threefold axis.

Thus, two kinds of molecular reorientation exist in the plastic phase: rotations of the whole molecule around a fourfold axis such as jumps of 90° permit alignment of the

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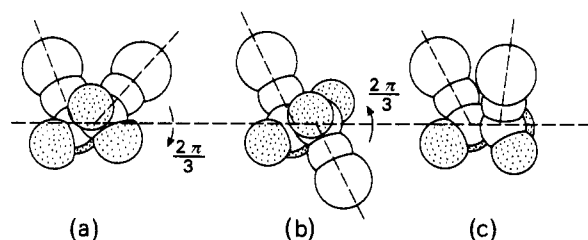


Figure 1. Schematic representation of t and g isomers.

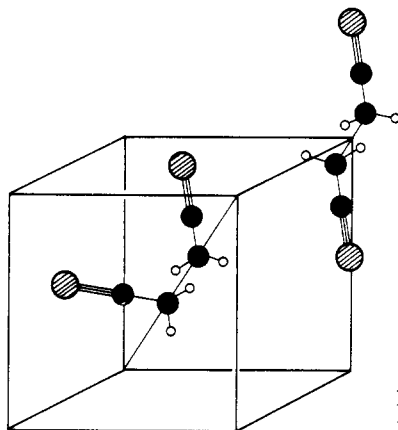


Figure 2. Example of molecular configurations in the cubic cell.

central C—C bond along another threefold axis of the cell; rotations of $\text{CH}_2\text{—C}\equiv\text{N}$ groups around a threefold axis and therefore such that one isomer is changed into another (the C—C \equiv N atoms thus lie in the (110) planes). As a result, each of the three possible molecular isomers can take 12 equilibrium configurations on each site.

Because of the disorder in such a plastic phase, the number of reflections is very small and the previous structure determination [1] was based on the measurement of seven independent reflections only. In the refinement, this fact requires strong constraints for the molecular degrees of freedom. The main constraint was that the central C—C bond was aligned along the threefold axis of the cell, whatever the isomeric conformation might be. The centres of mass of g isomers are thus situated at about 1.07 \AA from this axis. An isotropic temperature translational factor $\langle u^2 \rangle = 0.107 \text{ \AA}^2$ and a librational amplitude $\langle \omega^2 \rangle = 0.45 \text{ rad}^2$, corresponding to a libration of the $\text{CH}_2\text{—C}\equiv\text{N}$ group around the threefold axis, were obtained.

The present study was performed with a more powerful source using the multi-scan technique which enables 20 independent reflections to be measured. This allowed us to use more accurate models. Two methods were attempted: the first used the symmetry-adapted functions, and the second assumed discrete equilibrium orientations but an offset vector was introduced in order to localise more accurately the position of the centre of mass of the g isomers. A particular objective for this new determination is to provide structural data in a detailed analysis of the local order [10].

2. Experimental details

X-ray diffraction experiments were performed at room temperature ($T \approx 293 \text{ K}$) using an automatic four-circle diffractometer. The power of the x-ray source was 1500 W. A

pyrolytic graphite monochromator selected the Mo K α line ($\lambda = 0.7107 \text{ \AA}$). The sample was a single crystal grown by sublimation in a glass capillary (size, $0.3 \text{ mm} \times 0.3 \text{ mm} \times 0.4 \text{ mm}$). The intensity of each Bragg peak was measured within an angular range of 1.5° with a scan speed of $0.012^\circ \text{ s}^{-1}$. 61 reflections corresponding to 20 independent reflections were measured using the step scan method (ω scan) for θ between 2° and 22° . Because of the very poor intensity of most reflections, it was necessary to make a summation of up to 50 scans which corresponded to total counting times of about 2 h per reflection. During the experiment, no significant change in the three reference reflections was observed.

3. Data analysis

We verify that the sample is BCC, the angles being equal to $90^\circ (\pm 0.03^\circ)$; the lattice parameter was found to be equal to $a = 6.335 \text{ \AA}$ with a precision of $\pm 0.010 \text{ \AA}$ at $T \approx 293 \text{ K}$. The systematic extinction rules confirm the space group Im3m.

Considering the weak value of the linear absorption coefficient ($\mu = 0.75 \text{ cm}^{-1}$) and the small size of the sample, no absorption correction was made. The integrated intensities were corrected for the Lorentz–polarisation factors. The experimental structure factors were obtained using the program PROFILE [11]. Five of the 20 independent reflections were omitted in the refinements on the grounds that $F(I) < \sigma(I)$.

3.1. Expansion of $F(Q)$ in cubic harmonics

The probability density function for an atom k can be expanded into a set of site symmetry-adapted functions which are the cubic harmonics in the case of succinonitrile [12]:

$$a(\mathbf{r}, k) = \sum_{lm} a_{lm}^{(k)} K_{lm}(\Omega).$$

Here $\Omega = (\theta, \varphi)$ denotes the polar angles of \mathbf{r} . For rigid molecules, the coefficients $a_{lm}(k)$ are not independent. An expansion into the molecular symmetry-adapted functions $M_{lm'}(\mathbf{r}'_k)$ reads

$$a_{lm}^{(k)} = \sum_{m'} A_{mm'}^l M_{lm'}(\mathbf{r}'_k).$$

The coefficients $A_{mm'}^l$ express the orientational probability of the molecular axis system with respect to the crystallographic axes. A similar expansion has to be made for both t and g isomers. Moreover, the position of the centre of mass for g isomers is not imposed by the symmetry; it is the translation–rotation coupling that has to be taken into account [13].

We have adopted the following indexation of the atoms: $k = 1$ for the central carbon atoms, $k = 2$ for the carbon atoms of the nitrile groups and $k = 3$ for the nitrogen atoms. Owing to the low symmetry of the isomers, the expansion contains many non-zero terms m' for each order l . Since the molecule is deformable, one way to obtain the coefficients $A_{mm'}^l$ would be to consider the rigid body formed by the half-molecule $\text{CH}_2\text{—C}\equiv\text{N}$. In this case, the former system of equations cannot be solved since only two coefficients $a_{41}^{(k)}$, corresponding to $k = 2, 3$, were determined. Because of this, the relative atomic positions in the molecular system could not be considered and thus the *trans* and *gauche* configurations could not be distinguished. Therefore the geometry of the molecule

cannot be taken into account and the atoms are distributed on independent shells. So, for an atom k at ρ_k from the centre of mass of the molecule, we may write

$$a_{lm}^{(k)}(\mathbf{r}) = c_{lm}^{(k)} \delta(r - \rho_k) / r^2$$

where the coefficients $c_{lm}^{(k)}$ are the parameters to be refined.

If we neglect correlations between translational and rotational motions, the structure factor is given by [12]

$$F(\mathbf{Q}) = \exp[-W(\mathbf{Q})] \sum_{klm} i^l f_k(\mathbf{Q}) n_k c_{lm}^{(k)} j_l(\mathbf{Q}\rho_k) K_{lm}(\Omega_{\mathbf{Q}})$$

where the sum is extended over k spherical shells of radius ρ_k which are occupied by n_k equivalent atoms, $f_k(\mathbf{Q})$ is the scattering factor of atom k , $j_l(\mathbf{Q}\rho_k)$ denotes the spherical Bessel functions with the argument $(\mathbf{Q}\rho_k)$, the $c_{lm}^{(k)}$ are the expansion coefficients of the cubic harmonics $K_{lm}(\Omega_{\mathbf{Q}})$ which are invariant under all operations of the site symmetry, $\Omega_{\mathbf{Q}}$ denotes the polar angles of the scattering vector \mathbf{Q} in a coordinate system defined by the crystallographic axes and $\exp[-W(\mathbf{Q})]$ is the Debye–Waller factor for the molecular translational motion.

Owing to the symmetry invariance of $a(\mathbf{r}, k)$, only terms of order $l = 0, 4, 6, 8$ and $m = 1$ have to be considered. Taking into account the orthonormality condition of cubic harmonics, we have $c_{01}^{(k)} = 1$. In the case of succinonitrile, the structure factor thus may be written

$$F(\mathbf{Q}) = A \exp\left(-\frac{\mathbf{Q}^2 \langle u^2 \rangle}{2} \sum_{k=1}^4 f_k(\mathbf{Q}) n_k [j_0(\mathbf{Q}\rho_k) + c_{41}^{(k)} j_4(\mathbf{Q}\rho_k) K_{41}(\Omega_{\mathbf{Q}}) + c_{61}^{(k)} j_6(\mathbf{Q}\rho_k) K_{61}(\Omega_{\mathbf{Q}})]\right).$$

To minimise the number of parameters, the expansion is carried out up to the order $l = 6$. n_k is equal to 4 for hydrogen atoms and 2 for other atoms. Concerning the hydrogen atoms, only the order $l = 0$ for the Bessel functions was taken into consideration. A is a scale factor and $\langle u^2 \rangle$ the mean square amplitude of translation. Considering the weak number of reflections, assumptions about the bond lengths and the geometry of the molecule were made. The following interatomic distances were used [14]: C—C central, 1.541 Å; C—C in the nitrile group, 1.440 Å; C≡N in the nitrile group, 1.158 Å; C—H in the nitrile group, 1.115 Å. The C—C≡N group was assumed to be linear and the C—CH₂—C group to be a regular tetrahedra. The different radii were deduced to be $\rho_1 = 0.771$ Å for central carbon atoms, $\rho_2 = 1.846$ Å for other carbon atoms, $\rho_3 = 2.946$ Å for nitrogen atoms and $\rho_4 = 1.554$ Å for hydrogen atoms.

Because of the weak value of the scattering vector in x-ray diffraction data involving a small argument $(\mathbf{Q}\rho_1)$ in the Bessel functions $j_4(\mathbf{Q}\rho_1)$ and $j_6(\mathbf{Q}\rho_1)$, the coefficients $c_{41}^{(1)}$ and $c_{61}^{(1)}$ relative to the central carbon atoms could not be determined. The refinement procedure was performed using the least-squares method and a reliability factor R , defined as $\sum_i |F_{\text{obs}}(i) - F_{\text{calc}}(i)| / |F_{\text{obs}}(i)|$ and a weighted factor R_w , defined as $\sum_i W_i (|F_{\text{obs}}(i)| - |F_{\text{calc}}(i)|)^2 / \sum_i W_i |F_{\text{obs}}(i)|^2$ with $W_i = 1 / \sqrt{|F_{\text{obs}}(i)|^2}$ were calculated. The observed and calculated structure factors and the final parameters are reported in table 1. The very large mean square amplitude of translation ($\langle u^2 \rangle \approx 0.20$ Å²) is often a signature of positional disorder. Figure 3 shows the orientational probability of N(3) and C(2), i.e. atoms of nitrile group. It is clear that the nitrogen atoms are localised along the fourfold axis of the cell but large librational motions occur; the half-width at half-maximum of the orientational probability distribution is about 21°. The orientational probability of C(2) exhibits a negative part originating from an expansion up to the order

Table 1. Observed and calculated structure factors and final values of the different parameters (model with surface harmonics). The reflections marked with an asterisk (*) were not taken into account in the refinement.

<i>h k l</i>	F_{obs}	$\sigma(F_{\text{obs}})$	F_{calc}
1 1 0	6.236	0.005	6.302
2 0 0	7.171	0.006	7.141
2 1 1	0.773	0.003	0.702
2 2 0	0.677	0.002	0.628
3 1 0	0.620	0.003	0.585
2 2 2	0.129	0.003	0.118
3 2 1	0.064	0.007	-0.018
4 0 0	0.469	0.002	0.395
4 1 1	0.103	0.005	0.195
3 3 0	0.101	0.005	-0.124
4 2 0	0.032	0.029	0.047
3 3 2	0.038	0.022	0.052
4 2 2*	0.002	0.026	0.019
5 1 0	0.038	0.027	-0.070
4 3 1*	0.002	0.026	-0.018
5 2 1	0.059	0.018	-0.076
4 4 0*	0.002	0.050	-0.035
5 3 0*	0.002	0.051	-0.046
4 3 3*	0.002	0.051	-0.023
6 0 0	0.082	0.008	-0.067

	Value	Standard deviation
<i>A</i>	42.69	0.92
$\langle u^2 \rangle (\text{\AA}^2)$	0.20	0.01
$C_{41}^{(2)}$	1.06	0.06
$C_{61}^{(2)}$	0.42	0.09
$C_{41}^{(3)}$	1.07	0.04
$C_{61}^{(3)}$	-0.20	0.05
<i>R</i> (%)	3.5	
<i>R</i> _w (%)	4.2	

$l = 6$ which appears insufficient. The lack of more experimental information did not allow higher-order terms to be refined.

3.2. Discrete orientation model

The molecule of succinonitrile was presumed to be distributed in 36 equilibrium orientations (12 *trans* and 24 *gauche* configurations) weighted by the different proportions of the isomers [9]. The structure factor is expressed as an average on the orientations Ω_i :

$$F(\mathbf{Q}) = \sum_{\Omega_i} P(\Omega_i) F(\mathbf{Q}, \Omega_i)$$

where $F(\mathbf{Q}, \Omega_i)$ is the molecular structure factor corresponding to the molecule with the orientation Ω_i . Each *trans* configuration was weighted by $P(\Omega_t) = 0.23/12$ and each *gauche* configuration by $P(\Omega_g) = 0.77/24$.

To take into account the translation-rotation coupling, an offset parameter for the *g* isomers was used. Since the twofold molecular axis coincides with the twofold axis of

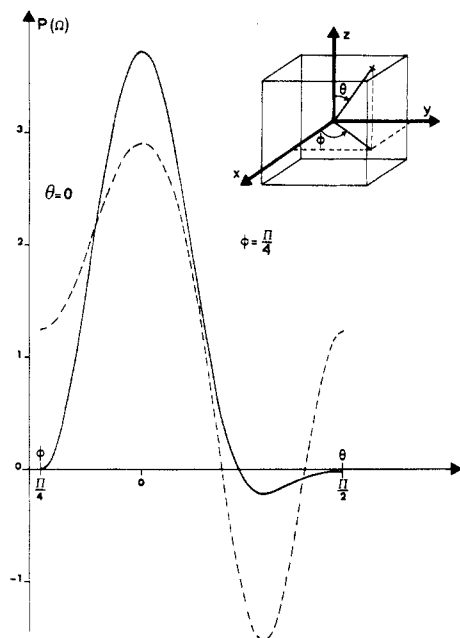


Figure 3. Orientational probability distribution of the nitrogen atoms (—) and the carbon atoms of the nitrile group (---).

Table 2. Atomic coordinates relative to a t isomer and a g isomer with $x_1 = 0.445 \text{ \AA}$, $x_2 = 0.17 \text{ \AA}$, $z_2 = 1.83 \text{ \AA}$, $x_3 = -0.055 \text{ \AA}$, $z_3 = 2.945 \text{ \AA}$, $x_4 = 0.23 \text{ \AA}$ and $z_4 = 1.52 \text{ \AA}$. The symmetry elements of the group $m\bar{3}m$ generate the equivalent equilibrium positions.

				t isomer			
C(1)	x_1	x_1	x_1	$C'(1)$	$-x_1$	$-x_1$	$-x_1$
C(2)	x_2	x_2	z_2	$C'(2)$	$-x_2$	$-x_2$	$-z_2$
N	x_3	x_3	z_3	N'	$-x_3$	$-x_3$	$-z_3$
H(1)	x_4	z_4	x_4	$H'(1)$	$-x_4$	$-z_4$	$-x_4$
H(2)	z_4	x_4	x_4	$H'(2)$	$-z_4$	$-x_4$	$-x_4$
				g isomer			
C(1)	$-x_1 - e$	$x_1 - e$	$-x_1$	$C'(1)$	$x_1 - e$	$-x_1 - e$	x_1
C(2)	$-x_2 - e$	$z_2 - e$	$-x_2$	$C'(2)$	$z_2 - e$	$-x_2 - e$	x_2
N	$-x_3 - e$	$z_3 - e$	$-x_3$	N	$z_3 - e$	$-x_3 - e$	x_3
H(1)	$-x_4 - e$	$x_4 - e$	$-z_4$	$H'(1)$	$x_4 - e$	$-x_4 - e$	z_4
H(2)	$-z_4 - e$	$x_4 - e$	$-x_4$	$H'(2)$	$x_4 - e$	$-z_4 - e$	x_4

the cell, an offset vector $e(\Omega_i)$ of the form $(-e, -e, 0)$ (and circular permutations) was introduced to make the centre of mass of g isomers coincide with the molecular site. In accordance with symmetry, the centre of mass of the t isomers was kept on the molecular site. The atomic coordinates relative to t and g configurations are given in table 2.

The position vector $r(k, \Omega_i)$ of atom k of the molecule with the orientation Ω_i with respect to the molecular site O is written (figure 4)

$$r(k, \Omega_i) = e(\Omega_i) + \mathbf{OG}'(\Omega_i) + r_G(k, \Omega_i)$$

where $\mathbf{OG}'(\Omega_i)$ denotes the position of the centre of mass of the molecule with respect to the origin when the central C—C bond coincides with the threefold axes of the cell and $r_G(k, \Omega_i)$ represents the position of the atom k with respect to the centre of mass of the molecule.

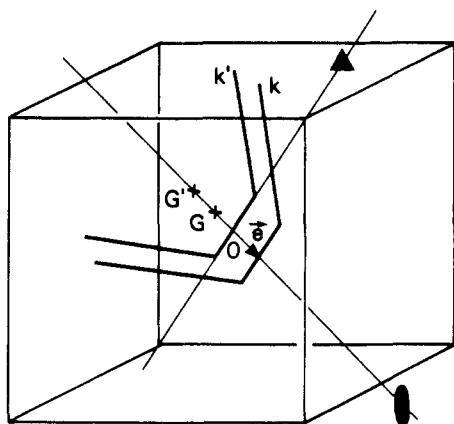


Figure 4. Schematic drawing of a *gauche* configuration showing the offset vector e along a two-fold axis. The primed molecule (Fontaine's model) is translated by e (present paper).

In the expression for the structure factor, the Willis–Pawley [15] correction was applied in order to take into account large-amplitude librations, yielding a term

$$\exp[i\mathbf{Q} \cdot \mathbf{r}_G(k, \Omega_i)(1 - \langle \omega^2 \rangle)].$$

The thermal agitation of the atoms is considered as an isotropic translation of the centre of mass of the molecule whatever its form and an isotropic libration of the molecule around its centre of mass. Thus the structure factor may be written as follows:

$$F(\mathbf{Q}) = A \exp\left(-\frac{\mathbf{Q}^2 \langle u^2 \rangle}{2}\right) \sum_{\Omega_i} \sum_k P(\Omega_i) f_k(\mathbf{Q}) \exp[i\mathbf{Q} \cdot \mathbf{r}_G(k, \Omega_i)] \\ \times (1 - \langle \omega^2 \rangle) + \mathbf{O}\mathbf{G}'(\Omega_i) + e(\Omega_i)] \exp\left(-\frac{|\mathbf{Q} \times \mathbf{r}_G(k, \Omega_i)|^2 \langle \omega^2 \rangle}{2}\right)$$

where A is a scale factor. In this expression there are four adjustable parameters: the scale factor A , the mean square translation amplitude $\langle u^2 \rangle$ and the mean square librational amplitude $\langle \omega^2 \rangle$ and the offset parameter e . In the refinement procedure, for a given e -value, the three other parameters were fitted. The final values of these parameters are summarised in table 3 for different values of e . In figure 5, R_w , $\langle u^2 \rangle$ and $\langle \omega^2 \rangle$ are reported as a function of the offset-vector component e . The best weighted reliability factor ($R_w = 8.85\%$) was obtained for $e = 0.30 \text{ \AA}$, which corresponds to a displacement of 0.42 \AA of the centre of mass for the *g* isomers. From table 2, we deduce that the average position of their centres of mass is at about 0.65 \AA from the molecular site. For this value, the final parameters are $\sqrt{\langle u^2 \rangle} = 0.52 \text{ \AA}$ and $\sqrt{\langle \omega^2 \rangle} = 10.1^\circ$ which show evidence of important vibrational motions. It is worth noting that the mean square translational amplitude $\langle u^2 \rangle$ is also minimal ($\langle u^2 \rangle = 0.267 \text{ \AA}^2$) for a value very close to that derived from R_w . The differences from Fontaine's results [1, 9] for $e = 0$ are essentially due to the Willis–Pawley correction that we use, which leads to a decrease in the librational amplitude. The observed structure factors and those calculated with $e = 0.30 \text{ \AA}$ are given in table 4. At large Bragg angles, the structure factors calculated with this model are smaller than those observed. The mean square amplitude of translation is probably somewhat overestimated. Because of the small number of observed reflections, additional parameters in the refinement were tried but without success. In particular, attempts were made to fit the ratios of isomer populations. Other refinements were performed considering a molecular libration around a threefold axis without improvement.

Table 3. Values of the mean square translational amplitude ($\langle u^2 \rangle$) and the mean square librational amplitude ($\langle \omega^2 \rangle$) and corresponding reliability factor R and weighted reliability factor R_w for different values of the offset parameter ($e, e, 0$).

e (Å)	$\langle u^2 \rangle$ (Å ²)	$\langle \omega^2 \rangle$ (rad ²)	R (%)	R_w (%)
0	0.392(88)	0.054(14)	14.94	15.24
0.05	0.356(74)	0.052(12)	13.73	14.12
0.10	0.327(64)	0.050(10)	12.38	12.94
0.15	0.303(54)	0.046(9)	11.30	11.59
0.18	0.287(48)	0.044(8)	10.64	10.75
0.20	0.279(45)	0.043(7)	10.20	10.22
0.25	0.268(39)	0.038(6)	9.04	9.18
0.28	0.267(38)	0.034(6)	8.30	8.88
0.30	0.270(38)	0.031(6)	7.77	8.85
0.32	0.274(39)	0.028(6)	7.32	8.98
0.36	0.286(43)	0.022(6)	7.70	9.63
0.40	0.294(49)	0.017(7)	8.67	10.64

3.3. Evaluation of the offset parameter from steric hindrance analysis

It was shown that, in the plastic phase of succinonitrile, there is complete hindrance between some orientational configurations of neighbouring molecules [16, 17]. We undertook a systematic analysis of the possible overlap of van der Waals spheres on the assumption of hard-core repulsions. We assumed that the offset parameter corresponds to positions of *gauche* configurations for which the overlap is minimal. More precisely, the calculated offset was obtained when the number of the hindered configurations between a molecule at the origin taken as reference and its first and second neighbours was a minimum. As mentioned in the above paragraph, the C—C≡N group was considered as linear, the C₃H₂ tetrahedra as regular and the offset vector along the twofold axis of the cell. From equilibrium positions of the molecule in the cell and van der Waals radii of atoms, the analysis of the steric hindrance shows the following.

(i) Between two second-neighbour molecules, 144 configurations among 1296 are hindered owing to the van der Waals sphere overlap of nitrogen atoms when these atoms are pointing at each other. For these hindered configurations, the distance between nitrogen atoms varies from 0.48 to 1.10 Å according to the isomers whereas the nitrogen van der Waals radius is 1.60 Å. It appears that the distance between two atoms is smaller than the sum of the van der Waals radii. The overlap is very strong so that the number of hindered configurations is not modified by the offset parameter value.

(ii) Between two first-neighbour molecules, the van der Waals spheres of carbon and nitrogen atoms of the nitrile groups overlap for some given orientations of both these molecules. Figure 6 shows clear evidence of a strong influence of the value of e on the number of the steric contacts: the impossibilities are minimal (444 hindered configurations among 1296) when the offset ($e, e, 0$) is such that $e = 0.36$ Å. This value is closer than those obtained from the structure using the Frenkel model. The large number of hindered configurations involving important spatial correlations should be noted.

4. Conclusion

The plastic phase of succinonitrile is characterised by a limited number of Bragg reflections. Therefore, only a few parameters could be refined: four in the case of the Frenkel model and six in the case of the surface-harmonics model.

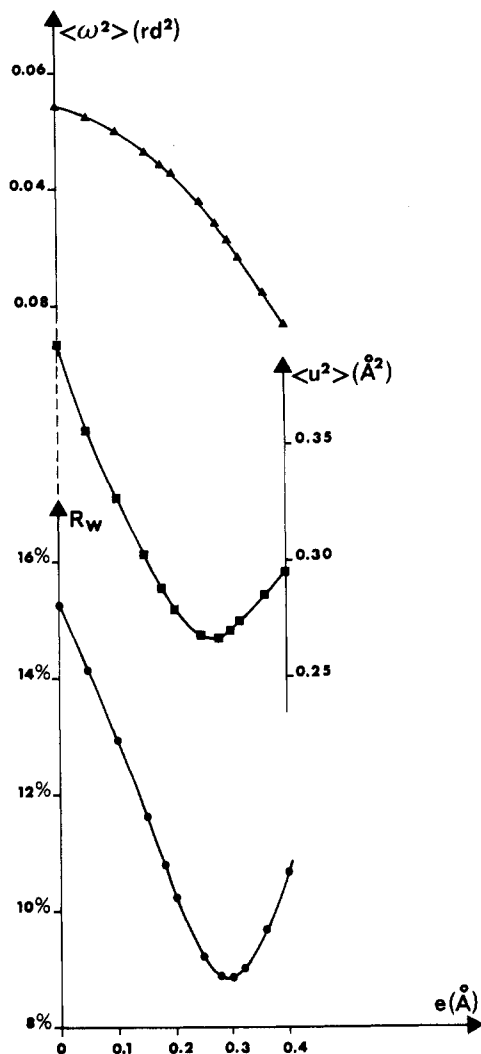


Figure 5. Isotropic temperature factor $\langle \omega^2 \rangle$ (\blacktriangle), $\langle u^2 \rangle$ (\blacksquare) and weighted reliability factor R_w (\bullet) as a function of the offset vector component e .

The determination of the structure of the plastic phase of succinonitrile by means of symmetry-adapted functions confirms that the orientational probability of nitrogen atoms is maximal along the [100] axis of the cubic cell. Nevertheless, their delocalisation is large since the half-width at half-maximum of the orientation probability curve in the (100) plane is about 21° . The isotropic mean square amplitude of translation was found to be 0.20 \AA^2 .

By the Frenkel model, the relaxed constraint that we were able to introduce in the refinement effectively shows that the centre of mass for the *gauche* conformations is nearer to the site than in the previous structure. An offset vector aligned along the twofold axis for the *g* isomers was found to have an amplitude equal to 0.42 \AA . The isotropic temperature factors are 0.27 \AA^2 for translational motions and 0.031 rad^2 for librational motions.

Both models provide large temperature factors which express significant disorder. From the analysis of the spatial siting of neighbouring molecules, we deduce a most probable offset value e of 0.36 \AA . Given the assumptions which were made about the

Table 4. Observed and calculated structure factors for $e = 0.30 \text{ \AA}$ (Frenkel model; $R = 7.8\%$; $R_w = 8.8\%$). The reflections marked with an asterisk (*) were omitted in the refinement.

$h k l$	F_{obs}	$\sigma(F_{\text{obs}})$	F_{calc}
1 1 0	6.530	0.005	6.429
2 0 0	7.510	0.006	7.592
2 1 1	0.809	0.003	-0.756
2 2 0	0.709	0.002	0.874
3 1 0	0.649	0.003	0.464
2 2 2	0.135	0.003	-0.237
3 2 1	0.067	0.007	-0.151
4 0 0	0.491	0.002	0.203
4 1 1	0.108	0.005	-0.082
3 3 0	0.105	0.005	0.039
4 2 0	0.034	0.030	0.010
3 3 2	0.040	0.023	-0.018
4 2 2*	0.002	0.027	-0.014
5 1 0	0.040	0.029	-0.007
4 3 1*	0.002	0.027	-0.011
5 2 1	0.062	0.019	-0.007
4 4 0*	0.002	0.052	-0.002
5 3 0*	0.002	0.053	-0.002
4 3 3*	0.002	0.053	0.000
6 0 0	0.085	0.008	-0.022

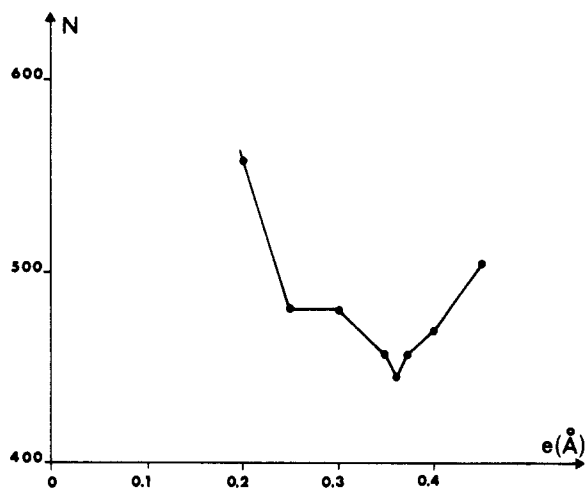


Figure 6. Number of hindered configurations between two first-neighbour molecules as a function of the offset vector component e .

geometry of the molecule, these results provided by both the geometrical analysis of the steric hindrance and the structure refinement by the Frenkel model are in quite good agreement. Moreover, steric effects have revealed important orientational correlations between first- and second-neighbour molecules.

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