# *On the Diffuse Scattering of X-Rays by Single Crystals of Tetranitromethane*[1]

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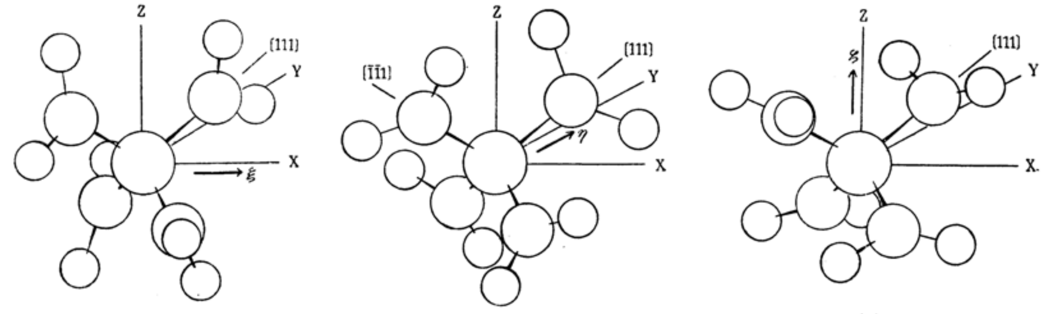
## Introduction

Oda, Iida, Watanabé and Nitta[3,4,5] reported the crystal structure of cubic tetranitromethane using Laue and oscillation photographic data ($a=7.08$ Å $Z=2$, $T^{3}_{\mathrm{d}}-I\bar{4}3\,m$). The observed high symmetry of the crystal, $T^{3}_{\mathrm{d}}-I\bar{4}3\,m$, was explained by a statistical arrangement of the atomic groups or molecules within the crystal. In other words, the central carbon atoms of the two molecules in the unit cell lie at the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the eight nitrogen atoms on the four body-diagonals with the C—N bond axes are parallel to each of the other molecules, the orientation of the pairs of oxygen atoms in the nitro groups being, however, in certain disorder around the respective C—N bond axis. The simplest model will be the one in which all the pairs of oxygen atoms rotate freely around the C—N bond axes. A calculation[5]* was carried out based on this model and the result explains well the observed intensities of Bragg reflections and the circular diffuse halo, the maximum occurring at 32° for Cu $K_{\alpha}$. In addition to



(a) (b) (c)

Fig. 1. The three different orientations of molecules in the crystal

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[3] T. Oda, T. Iida and I. Nitta, *J. Chem. Soc. Japan*, **64**, 616 (1943).

[4] T. Oda and T. Watanabé, *J. Chem. Soc. Japan*, **65**, 154 (1944). see also: P. H. Lindenmeyer and P. M. Harris, *J. Chem. Phys.*, **21**, 408 (1953).

[5] T. Oda and I Nitta, *J. Chem. Soc. Japan*, **65**, 621 (1944).

*) The calculation has given the x-ray diffuse scattering expressed by

$$N(K^{\circ}-K')=Nf^{2}_{\mathrm{o}}\{8+\sum_{\mathrm{n}}^{1,2,3,4}2J_{0}(2c_{\mathrm{n}})-\sum_{\mathrm{n}}^{1,2,3,4}4J_{0}^{2}(c_{\mathrm{n}})\}, \qquad (1)$$

in which $N$ is the number of molecules, $f_{\mathrm{o}}$ the atomic structure factor for oxygen, $J_{0}(c_{\mathrm{n}})$ the Bessel function of the zeroth order with the argument $c_{\mathrm{n}}$, $c_{\mathrm{n}}$ being

$$c_{\mathrm{n}}=4\pi(\rho/\lambda)\sin(\chi/2)\sin(\alpha_{\mathrm{n}}).$$

where $\chi$ is the scattering angle, $\alpha_{\mathrm{n}}$ the angle between the reflecting plane and the plane of the two rotating oxygen atoms in the n-th nitro group in the molecule, $\rho$ the radius of the oxygen orbit. It may be added here that this equation is essentially the same as the one (4.237) in Zachariasen's "*Theory of X-Ray Diffraction in Crystals*", 1945 p. 224.

these spot-like diffuse scattering was observed. In this paper we will show a more detailed analysis of the structure taking into consideration the mutual correlation between molecules, which enables us to explain such spot like diffuse scattering.

## Theoretical

We shall assume, to simplify matters, a flat-shaped molecule having the symmetry $D_{2d}-\bar{4}2\,m$ (Fig. 1 (a), (b), (c)) which is not very different from the model given by Stosick[6] from his electron diffraction study on gaseous tetranitromethane. We shall take the $X$-axis in Fig. 1 (a), which is the four-fold alternating axis of the symmetry $D_{2d}-\bar{4}2\,m$, as the molecular axis. It can be shown that by the simultaneous rotation of the four nitro groups, the molecular axis will be brought into $Y$-(Fig. 1 (b)) or $Z$-axis (Fig. 1 (c)), the positions of the nitrogen atoms remaining unchanged.

Let us denote by $P_l(x_0x_l)$ the probability that the orientational character of the molecule at the $l$-th lattice point will be of the kind $x_l$, when the one at the origin is of the kind $x_0$. We shall normalize $P_l(x_0x_l)$ as

$$\sum_{x_0} P_l(x_0x_l)=\sum_{x_l} P_l(x_0x_l)=1 \quad .$$

Since, in the present case, $x$ is assumed to possess three possibilities corresponding to molecular orientation in the directions of $X$, $Y$ and $Z$ axes, we shall designate them further as $\xi$, $\eta$ and $\zeta$. As the averaged crystal structure is a body-centered one, there are eight nearest lattice points about the $l$-th lattice point, which we shall designate as 1, 2, 3,$\cdots$, $\mu$,$\cdots$,8. The probability $W(x_1x_2\cdots x_\mu\cdots x_8\,;x_l)$ that the $l$-th is of the kind $x_l$ if the ones surrounding it are of the kinds $x_1$, $x_2$,$\cdots$,$x_\mu$,$\cdots$,$x_8$ is now introduced. Then

$$P_l(x_0x_l)=\sum_{x_1}^{\xi,\eta,\zeta}\cdots\sum_{x_8}^{\xi,\eta,\zeta}\prod_{\mu=1}^{8} P_\mu(x_0x_\mu)W(x_1x_2\cdots x_\mu\cdots x_8\,;x_l) \qquad \cdots\cdots(2)$$

When correlation is not large, $P_l(x_0x_l)$ will take a finite value, 1/3, for large value of $l$.

Introducing,

$$P_l(x_0x_l)=(1/3)+R_l(x_0x_l),$$

and using the normalization condition for $W(x_1\cdots x_\mu\cdots x_8\,;\,x_l)$,

$$\sum_{x_1}\cdots\sum_{x_8}\left(\frac{1}{3}\right)^8 W(x_1\cdots x_\mu\cdots x_8\,;x_l)=\frac{1}{3},$$

it follows that, dropping the suffix zero of $x_0$,

$$R_l(x\,x')=\sum_{\mu=1}^{8}\sum_{x''}^{\xi,\eta,\zeta}R_\mu(x\,x'')A_\mu(x''\,x')+N_l(x\,x'), \cdots(3)$$

in which

$$A_\mu(x''\,x')=\sum_{x''_1}\cdots\sum_{x''_{\mu-1}}\;\sum_{x''_{\mu+1}}\cdots\sum_{x''_8}\left(\frac{1}{3}\right)^{8-1}W(x''_1x''_2\cdots x''_{\mu-1}x''x''_{\mu+1}\cdots x''_8\,;x'),$$

where $\sum_{x''_1}\cdots\sum_{x''_8}$ means that the summation is to be carried out over three orientations for each of the seven molecules surrounding the $l$-th lattice point, the $\mu$-th neighbouring molecule being fixed to the orientation $x''$. In other words, $A_\mu(x''x')$ means the probability that the molecule at the $l$-th lattice point is of the kind $x'$ when the one at the $\mu$-th neighbouring point is of the kind $x''$. $N_l(x\,x')$ is the non-linear term of $R_l(x\,x')$.

Expressing the potential energy between two neighbouring molecules by $V_\mu(x''x')$, it is easily shown by symmetry consideration that

$$V(\xi,\xi)=V(\eta,\eta)=V(\zeta,\zeta)$$
$$V(\xi,\eta)=V(\xi,\zeta)=V(\eta,\xi)=V(\eta,\zeta)=V(\zeta,\xi)=V(\zeta,\eta).$$

Since $A_\mu(x''x')$ is expected to be proportional to the Boltzman factor $\exp\{-V_\mu(x''x')/kT\}$, we may assume that

$$A(\xi,\xi)=A(\eta,\eta)=A(\zeta,\zeta)=(1+2\alpha)/3,$$
$$A(\xi,\eta)=A(\xi,\zeta)=A(\eta,\xi)=A(\eta,\zeta)=A(\zeta,\xi)$$
$$=A(\zeta,\eta)=(1-\alpha)/3,$$

where $\alpha$ is a function depending upon potential and temperature.

Let $\mathbf{b}=(\sigma-\sigma_0)/\lambda$ where $\lambda$ is the wave length of the x-rays, $\sigma_0$ and $\sigma$ the unit vectors expressing the directions of the incident and scattered rays. The averaged intensity of scattered x-rays will be given by

$$<I(\mathbf{b})>_{\mathrm{Av.}}=\sum_{l}\sum_{l'}\sum_{x_l}\sum_{x_{l'}}(1/3)P_{l'-l}(x_lx_{l'})f(x_l)f^*(x_{l'})\exp\{2\pi i(\mathbf{b},\mathbf{r}_{ll'})\}, \qquad \cdots\cdots(4)$$

where $f(x_l)$ represents the " molecular " structure factor for the molecule at the $l$-th lattice point and $\mathbf{r}_l$ its position vector, $\mathbf{r}_{l\,l'}$ being $\mathbf{r}_l-\mathbf{r}_{l'}$. This equation can be put into the following form[7],

$$<I(\mathbf{b})>_{\mathrm{Av.}}=I_1(\mathbf{b})+I_2(\mathbf{b}), \qquad \cdots\cdots(5)$$

in which

$$I_1(\mathbf{b})=\mathrm{Spur}(\boldsymbol{F}\,\boldsymbol{S}_0),\ I_2(\mathbf{b})=\mathrm{Spur}(\boldsymbol{F}\boldsymbol{S}_1), \qquad \cdots\cdots(6)$$

$$\boldsymbol{S}_0=\left(\frac{1}{3}\right)^2\boldsymbol{I}\sum_{l}\sum_{l'}\exp\{2\pi i(\mathbf{b},\ \mathbf{r}_{ll'})\} \qquad \cdots\cdots(7)$$

$$\boldsymbol{S}_1=\frac{1}{3}N\sum_{l}\boldsymbol{R}_l\exp\{-2\pi i(\mathbf{b},\ \mathbf{r}_l)\}, \qquad \cdots\cdots(8)$$

$\boldsymbol{I}$ being a matrix whose elements are all one, $\boldsymbol{R}_l$ a matrix whose elements are $R_l(x\,x')$ and $N$ the number of molecules in the crystal. $\boldsymbol{F}$ is a matrix whose elements are products of two " molecular " structure factors for the various orientations. In the present case

$$\boldsymbol{F}=\begin{pmatrix} f_\xi^*f_\xi & f_\xi^*f_\eta & f_\xi^*f_\zeta \\ f_\eta^*f_\xi & f_\eta^*f_\eta & f_\eta^*f_\zeta \\ f_\zeta^*f_\xi & f_\zeta^*f_\eta & f_\zeta^*f_\zeta \end{pmatrix}$$

In (5) $I_1$ stands for the Laue-Bragg scattering and $I_2$ for the diffuse scattering. Since $\boldsymbol{R}_l$ tends to zero for large value of $l$, it is possible[8] to calculate (8) and (6) by an approximate estimation of $R_l$ for small values of $l$.

From (3) one finds, by introducing matrices $\boldsymbol{A}_\mu$ and $\boldsymbol{N}_l$ whose elements are $A_\mu(x''\,x')$ and $N_l(x\,x')$ respectively, the following expression,

$$\boldsymbol{R}_l=\sum_{\mu=1}^{8}\boldsymbol{R}_\mu\boldsymbol{A}_\mu+\boldsymbol{N}_l,$$

or, noting that $\boldsymbol{R}_\mu\boldsymbol{I}=0$,

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[6] A. J. Stosick, *J. Am. Chem. Soc.*, **61**, 1127 (1939).

[7] T. Matsubara, *X-Rays*, **6**, 15 (1950).

[8] T. Oda, *X-Rays*, **5**, 95 (1949).

$$\boldsymbol{R}_l=\sum_{\mu}\boldsymbol{R}_\mu\boldsymbol{A}'_\mu+\boldsymbol{N}_l, \qquad \cdots\cdots(9)$$

where

$$\boldsymbol{A}'_\mu=\boldsymbol{A}_\mu-\frac{1}{3}\boldsymbol{I}.$$

In the present case, $\mathbf{A}'_\mu$ is independent of $\mu$ and equal to

$$\boldsymbol{A}'=\frac{\alpha}{3}\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}$$

The summation over $l$ of (9) multiplied by $\exp\{-2\pi i(\mathbf{b},\ \mathbf{r}_l)\}$ gives

$$\boldsymbol{S}_1=N\boldsymbol{M}(\boldsymbol{E}-\boldsymbol{B})^{-1}, \qquad \cdots\cdots(8')$$

where $\boldsymbol{E}$ is the unit matrix, and

$$\boldsymbol{B}=\sum_{\mu=1}^{8}\varepsilon_\mu\boldsymbol{A}'_\mu, \quad \varepsilon_\mu=\exp\{-2\pi i(\mathbf{b},\ \mathbf{r}_\mu)\},$$

$\mathbf{r}_\mu$ being a position vector expressing one of the eight lattice points measured from their central point, and

$$\boldsymbol{M}=\frac{1}{3}\sum_{l}\boldsymbol{N}_l\exp\{-2\pi i(\mathbf{b},\ \mathbf{r}_l)\}. \qquad \cdots\cdots(10)$$

In this case $\boldsymbol{B}$ is given by

$$\boldsymbol{B}=8(\cos\pi H\cos\pi K\ \cos\pi L)\boldsymbol{A}',$$

where $H=(\mathbf{b},\ \mathbf{a}_1)$, $K=(\mathbf{b},\ \mathbf{a}_2)$, $L=(\mathbf{b},\ \mathbf{a}_3)$ corresponds to a point in the reciprocal space, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ being the cubic vector set.

By transforming $\boldsymbol{B}$ into the diagonal matrix, $I_2(\mathbf{b})$ is expressed as follows:

$$I_2(\mathbf{b})=N\sum_{i=1}^{3}\frac{m_{ii}}{1-\lambda_i}$$

where $\lambda_1=0$, $\lambda_2=\lambda_3=8\alpha\cos\pi H\cos\pi K\cos\pi L$, and $m_{ii}$ corresponds to diagonal elements of the matrix $\boldsymbol{UFMU}^{-1}$ or $\boldsymbol{UFU}^{-1}\ \boldsymbol{UMU}^{-1}$, $\boldsymbol{U}$ being unitary and

$$\boldsymbol{U}=\begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 1/\sqrt{6} & -2/\sqrt{6} & 1/\sqrt{6} \end{pmatrix}$$

which has been used in the diagonalization of $\boldsymbol{B}$. $\boldsymbol{UFU}^{-1}$ is calculated as

$$\begin{pmatrix} (1/3)\,|f_\xi+f_\eta+f_\zeta|^2 & (1/\sqrt{6})\,(f_\xi^*+f_\eta^*+f_\zeta^*)\,(f_\xi-f_\zeta) & (1/\sqrt{23})\,(f_\xi^*+f_\eta^*+f_\zeta^*)\,(f_\xi+f_\zeta-2f_\eta) \\ (1/\sqrt{6})\,(f_\xi^*-f_\zeta^*)\,(f_\xi+f_\eta+f_\zeta) & (1/2)\,|f_\xi-f_\zeta|^2 & (1/2\sqrt{3})\,(f_\xi^*-f_\zeta^*)\,(f_\xi+f_\zeta-2f_\eta) \\ (1/3\sqrt{2})\,(f_\xi^*+f_\zeta^*-2f_\eta^*)\,(f_\xi+f_\eta+f_\zeta) & (1/2\sqrt{3})\,(f_\xi^*+f_\zeta^*-2f_\eta^*)\,(f_\xi-f_\zeta) & (1/6)\,|f_\xi+f_\zeta-2f_\eta|^2 \end{pmatrix}$$

If we neglect all higher terms except the one for $l=0$ in (10), $\boldsymbol{M}$ and $\boldsymbol{UMU}^{-1}$ are given as follows:

$$\boldsymbol{M}\doteq(1/3)\boldsymbol{N}_0 \text{ and } \boldsymbol{N}_0=\boldsymbol{R}_0-\sum_{\mu=1}^{8}\boldsymbol{R}_\mu\boldsymbol{A}'.$$

$\boldsymbol{R}_0$ can be written as

$$\boldsymbol{R}_0=\boldsymbol{E}-(1/3)\boldsymbol{I}=\frac{1}{3}\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}.$$

Hence, if we take $\boldsymbol{R}_\mu=\boldsymbol{R}_0\boldsymbol{A}'$, $\boldsymbol{UMU}^{-1}$ becomes

$$\boldsymbol{UMU}^{-1}=\begin{pmatrix} 0 & 0 & 0 \\ 0 & m'_{22} & 0 \\ 0 & 0 & m'_{33} \end{pmatrix},$$

where $m'_{22}=m'_{33}=(1-8\alpha^2)/3$. From these calculations it follows that

$$I_2(\mathbf{b})=N\left(\frac{1}{3}\right)^2(1-8\alpha^2)$$

$$\frac{|f_\xi-f_\eta|^2+|f_\xi-f_\zeta|^2+|f_\eta-f_\zeta|^2}{1-8\alpha\cos\pi H\cos\pi K\cos\pi L}, \qquad \cdots\cdots(11)$$

where

$$f_\xi-f_\eta=f_0\{(C_\xi-C_\eta)+i(S_\xi-S_\eta)\},$$
$$f_\xi-f_\zeta=f_0\{(C_\xi-C_\zeta)+i(S_\xi-S_\zeta)\},$$
$$f_\eta-f_\zeta=f_0\{(C_\eta-C_\zeta)+i(S_\eta-S_\zeta)\},$$

and

$$C_\zeta=\ 4\cos2\pi Lz(\cos2\pi Hx\cos2\pi Ky+\cos2\pi Kx\cos2\pi Hy)$$

$$S_\zeta=-4\sin2\pi Lz(\sin2\pi Hx\sin2\pi Ky+\sin2\pi Kx\sin2\pi Hy),$$

$f_0$ being the atomic structure factor for oxygen atoms and $x$, $y$, $z$ its parameters.

## Discussion of the Results

When $\alpha=0$, $I_2(\mathbf{b})$ becomes

$$N(1/3)^2\{|f_\xi-f_\eta|^2+|f_\xi-f_\zeta|^2+|f_\eta-f_\zeta|^2\}, \quad \cdots(12)$$

or

$$N\{(1/3)(|f_\xi|^2+|f_\eta|^2+|f_\zeta|^2)-|(f_\xi+f_\eta+f_\zeta)/3|^2\}.$$

This last equation is equivalent to

$$N\{<|f(x)|^2>_{\text{Av.}}-|<f(x)>_{\text{Av.}}|^2\},$$

which was derived in the previous paper⁵⁾ dealing with free axial rotation of nitro-groups. These equations account well for the observed halo-type diffuse scattering.

Now we will discuss the case where $\alpha\neq0$. Since there is no long-range order with respect to molecular orientation, the correlation between neighbouring molecules would be small, in other words, the value of $|\alpha|$ will not be large. So we may assume $1>8|\alpha|$. The sign of $\alpha$ depends upon the interaction energy $V(xx')$ between two neighbouring molecules. For example if $V(\xi,\ \xi)>V(\xi,\ \eta)$, then $\alpha<0$, and on the other hand if $V(\xi,\ \xi)<(\xi,\ \eta)$, then $\alpha>0$.

Since the function

$$|f_\xi-f_\eta|^2+|f_\xi-f_\zeta|^2+|f_\eta-f_\zeta|^2 \qquad \cdots\cdots(12')$$

changes slowly with $\mathbf{b}$, one finds that the sharp maxima of $I_2$ $(\mathbf{b})$ occur in the directions for which $1-8\alpha\cos\pi H\cos\pi K\cos\pi L$ possesses minimum value. When $\alpha<0$, such directions are given by $H, K, L$ with integers and $H+K+L=2n+1$. When $H, K, L$ are integers, we have $H=h$, $K=k$ and $L=l$. However diffuse spots associated with {110}, and {112} (Table I) appeared. Hence, the assumption that $\alpha$ is negative leads to disagreement with the observation, provided that the observed diffuse spots are to be explained only by the correlation of the orientations of molecules, disregarding the influence of thermal motions. On the other hand if we take $\alpha>0$, then the maxima of $I_2$ (**b**) occur for the directions **b**(corresponding to $h+k+l=2n$), in agreement with the observation.

TABLE I

OBSERVED INTENSITIES OF MAXIMA OF THE DIFFUSE SPOTS WITH THE DIRECTIONS $H=h$, $K=k$ AND $L=l$ AND THEIR CALCULATED VALUES

| *HKL* | Obs. | Calc.* |
|---|---|---|
| 110 | st. | 29.6 |
| 200 | w. | 0.9 |
| 112 | st. | 19.2 |
| 220 | w. | 12.0 |

* In the calculation the polarization and the usual temperature fators have been also taken into account, $B$ in $\exp\{-B\sin^2(\chi/2)\}$ being given as 3.

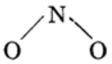
We may assume that the potential energies $V(x\,x')$ depend primarily upon the interaction between oxygen atoms of neighbouring molecules. The calculation of the distances between these oxygen atoms was carried out, taking the bond distances of C—N, N—O as 1.47, 1.21 Å and the bond angle  $\angle\mathrm{O{-}N{-}O}$ as 127°. The results are shown in Table II. In this case, we could expect that the potential energies for the two kinds of mutual orientations would not differ very much, so that $|\alpha|$ would be of a small value. It is, however, difficult to decide conclusively from such a qualitative consideration which one of these two is more stable and has a higher probability.

TABLE II

CALCULATED VALUES OF THE INTERMOLECULAR ATOMIC DISTANCES BETWEEN OXYGEN ATOMS

| I | II |
|---|---|
| 2.73 Å | 2.92 Å |
| 2.73 | 3.12 |
| 3.69 | 3.44 |
| 3.69 | 3.67 |
| 3.96 | 3.69 |
| 3.96 | 3.96 |

I stands for the parallel orientation $\xi, \xi$ and II for the perpendicular $\xi, \eta$.

In the theory stated above, it is seen that when $\alpha>0$, the maxima depend upon the values of (12′). In Table I are tabulated the calculated values of this equation, with the parameter values $x=0.28$, $y=0.11$, $z=0.16$ which are close to those $x=0.2675$, $y=0.054$, $z=0.1607$ derived from the bond-lengths and bond-angles as mentioned above. As is seen the calculation explained qualitatively the observed results. Further approximation will be attained by examination of the more appropriate model[4,6] of the molecule having the symmetry $S_4$—$\bar{4}$ and by taking into consideration of the lattice vibrations[9].

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[9] H. Faxén, *Z. Physik*, **17**, 266 (1923). I. Waller, *Z. Physik*, **17**, 398 (1923). W. H. Zachariasen, *Phys. Rev.* **57**, 597 (1940); **59**, 860 (1941). G, H. Beglie and C. M. Born, *Proc. Roy. Soc.* A **188**, 179, 189 (1947).