

Use of the Neutron Time-of-Flight Technique for Structure Investigations

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Abstract

The application of a time-of-flight neutron diffractometer for crystallographic investigations, designed on the basis of a pulsed neutron source, is discussed. The procedure for obtaining integrated intensities and introducing corrections is described. The results of a test experiment with perdeuterionaphthalene are given. The deuterium atom positions in the structure of $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{D}_2\text{O}$ are also refined and compared with those obtained using X-ray diffraction techniques. The observed systematic differences in bond lengths and valence angles are explained by the differences between the 'X-ray' and 'neutron' coordinates of the light atoms.

1. Introduction

In recent years papers describing the application of the neutron diffraction method to investigations of structures of complex (including biological) crystals have been published (Hodgkin, 1967; Schoenborn, 1969; Schoenborn, Nunes & Nathans, 1970). The main drawback in performing such experiments on a large scale is the low efficiency of conventional diffractometers employing a monochromatic neutron beam. Even in cases where neutron diffraction is used only to refine and complement X-ray data, one needs to increase the data-collection rate. The common feature of the new methods which have recently appeared (Nunes, Nathans & Schoenborn, 1971; Hubbard, Quicksall & Jacobson, 1972) is the use of a neutron spectrum of much larger energy range than that used in conventional diffractometers, resulting in a marked increase in the data-collection rate. Apparently, time-of-flight (TOF) diffractometers may have the best prospects for neutron investigations of protein crystal structures, since they combine high efficiency, good resolution and simplicity of analysis of the spectra measured. The applicability of the TOF method to structural investigations was discussed by Niç, Papulova, Sosnowskaja & Sosnovskij (1964); Buras, Mikke, Lebech & Leciejewich (1965) and Day & Sinclair (1970). In particular, it was shown by Bally, Chirtoc, Gheorghiu, Popovic, Stoica, Tarina & Balagurov (1975) and Cser (1976) that a powerful

high-flux pulsed neutron source and a multidetector system can provide much information from a protein crystal after several days of measurements. However, only a few quantitative TOF experiments with single crystals have so far been performed. This is due both to the low power of existing neutron pulsed sources and to some difficulties in the use of TOF diffractometers in comparison with conventional ones. The main problem of increasing the power of the source has recently been solved (Shabalin, 1976; Carpenter, 1977). Another problem – the lack of a large memory for storing and processing the experimental data – is also temporary. It can be shown (Bally *et al.*, 1975) that, if the TOF measurement acquires the information straightforwardly in terms of a reciprocal lattice, the memory capacity of a modern minicomputer is quite sufficient for the simultaneous observation of several dozen diffraction maxima. Other difficulties involve the need to take wavelength-dependent factors into account: namely, extinction and absorption in the sample and the effective neutron spectrum. In the analysis of simple structures the worst complications are mainly due to extinction. However, this effect becomes less serious with increasing structural complexity because the average structure factors decrease. Statistical analysis (Bally *et al.*, 1975) of the structure factors of myoglobin crystals used in the experiments of Schoenborn (1969) has shown that in a group of 10^4 reflections only 7.5% have an extinction correction greater than 1%. The method of correcting for neutron absorption is simple, hence the main remaining difficulty is taking into account the effective spectrum. Another problem is that of obtaining the integrated intensities of the diffraction maxima. Conventional methods based on a representation of the diffraction spectrum by an analytical function do not give the required accuracy with TOF diffractometers owing to the complicated shape of the maxima and background.

In this paper, results are given of the first experiments with the TOF neutron diffractometer constructed in the Laboratory of Neutron Physics of JINR for use with the IBR-30 pulsed reactor.

The experiments may be divided into three groups. (1) Measurements with polycrystalline V and Mo carried out to define the effective neutron spectrum and to estimate the systematic errors in its description.

(2) Measurements with a crystal of perdeuterio-naphthalene, $C_{10}D_8$, the structure of which is well known, to elucidate the accuracy of structure factor determination in the case of crystals as well as to obtain them from the diffraction spectra. (3) The technique was then used in the analysis of the results of an experiment with a crystal of deuterated lanthanum magnesium nitrate, $La_2Mg_3(NO_3)_{12} \cdot 24D_2O$ (LMN), the main purpose of which was to refine the positions of the D atoms.

2. Experimental

The measurements have been made with a conventional scheme for time-of-flight diffraction investigations (with one of the beams of the IBR-30). The operation of the reactor and its beam characteristics have been described in detail by Frank (1972). The geometry of the experiment is shown in Fig. 1. The diffractometer itself is a massive metallic plate with a three-axis GKS-100 goniometer and a detector on a movable arm. The scattering angle could be varied from -30° to 210° with a setting accuracy of about $2'$. The major part of the flight path was evacuated. A battery of enriched BF_3 counters with a window 30×50 mm served as a detector. Some measurements were performed with 3He counters. The average reactor power during the measurements was about 15 kW. The neutron time-of-flight spectra were registered with a multichannel TOF analyzer and were recorded on magnetic tape. A good time resolution due to the long flight path allowed simultaneous observation of a sufficient number of peaks. For example, in the spectrum of polycrystalline Mo measured at a scattering angle of 146° , 25 maxima were processed with the limiting hkl being 721. A more detailed description of the experimental technique and the sample characteristics is given by Balagurov, Borca, Dlouha & Mironova (1977).

3. A method for obtaining the integrated intensities of the diffraction maxima

Recently, in order to obtain integrated intensities, profile analysis of the whole spectrum or some part of it

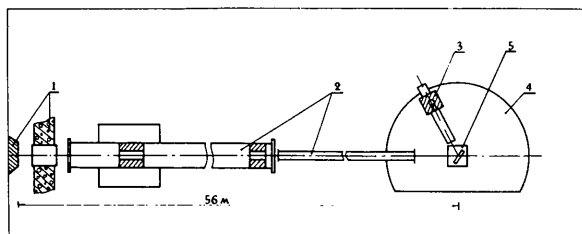


Fig. 1. Experimental set up: (1) neutron moderator, and biological shielding; (2) vacuum and argon neutron guides with collimators; (3) detector; (4) a plate with a movable arm; (5) goniometer with a sample.

has been used (Rietveld, 1969; Windsor, 1975). A description of the diffraction maxima (peaks) and background is given by the function

$$F(x, Q) = \sum_i \varphi_i(x, Q) + B(x, Q), \quad (1)$$

where x is the channel number of the analyzer, φ_i and B are the analytical functions for the peaks and the background, which depend on a set of parameters Q .

The main difficulty of this approach is determination of the functions φ_i and B . In order to obtain unbiased Q parameter estimates, the functions φ_i and B should correspond as closely as possible to the real peaks and background; further, no strong correlation between parameters should exist. These requirements are easily satisfied only for peaks of a rather simple shape, e.g. Gaussian, which are completely characterized by the three parameters: amplitude, position and width. For peaks of a more complicated shape one must introduce a large number of parameters; nevertheless, all the factors often fail to be taken into account, e.g. a non-Gaussian distribution of mosaic block orientations in a single crystal, a significant contribution of quasielastic scattering, local background fluctuations, etc.

Inexact φ_i and B functions, and correlation between the parameters in (1) cause systematic errors of the quantities to be determined (e.g. the integrated peak intensities) which may outweigh their statistical errors. We have developed a method for the determination of the principal spectral peak characteristics which does not imply a knowledge of the parametrical functions φ_i and B (Zlokazov, 1975). The peak shape (as well as background) is determined experimentally. The measured histogram was made a smooth function by parabolic interpolation. Considering this curve as a model for the real peak we normalize it in such a way that it has a position equal to 0, with area and width equal to 1.

Furthermore, an assumption is made that the real object and its model are connected by a definite functional dependence

$$r(x) = \hat{T}m(x) \quad (2)$$

[here $r(x)$, \hat{T} and $m(x)$ denote a real object, an operator and a model respectively] such that a set of $\{\hat{T}\}$ satisfies only some definite conditions and through that forms a definite transformation class. By linear transformation, an expression of the type (2) was obtained as follows (Zlokazov, 1977):

$$r(x, A, P, W) = Am \left(\frac{x - P}{W} \right). \quad (3)$$

The meaning of statement (3) is clarified as follows: a real object r is the model m , shifted by P channels, broadened by the width W and amplified by the similarity coefficient A . If the model is normalized as

above, then A is the amplitude, P the position, and W the width of the peak.

Computation of the values A_i , P_i , W_i is performed with a conventional least-squares-refinement procedure. The partial derivatives with respect to these parameters are calculated from an algorithm based on relation (3). The real single diffraction maxima obtained with good statistics are most suitable for a peak model $m(x)$.* Such a model seems to take all the peculiarities of the shape of the maximum into account.

This method assumes that no characteristics other than A , P and W change values along the spectrum. If this is not the case (e.g. the peak asymmetry varies), the spectrum is partitioned into intervals within which only A , P and W may be regarded as variables and for every such interval its own model is introduced.

This method is implemented in a Fortran subroutine (Zlokazov, 1978) for the BESM-6 and CDC-6500 computers. It takes 1 s for the CDC-6500 computer to process one peak. A more detailed consideration of the method and examples of processing are given by Balagurov, Dlouha, Mironova & Zlokazov (1979).

4. Determination of the effective spectrum

A combined method was used, for the determination of the effective neutron spectrum, which was based on a parametrical function description. The parameters of this function are initially found from measurements made on an incoherent scatterer and on a polycrystalline sample. They are then refined in the single-crystal data analysis. We used a six-parameter function:

$$\Phi(\lambda) = \Phi_0(e^{-C_1^2/\lambda^2}/\lambda^{C_2})e^{-C_3\lambda - C_4\Sigma_{\text{coh}}(\lambda)}(1 - e^{-C_5\lambda}), \quad (4)$$

where Φ_0 , and C_1 to C_5 are the parameters. The expression in this first set of parentheses modifies the Maxwell spectrum shape; this is followed by an exponent which takes into account the relaxation of the neutron beam in air and the Al windows of the neutron guide; $\Sigma_{\text{coh}}(\lambda)$ is the macroscopic integral coherent cross section of Al; and the final term takes into account the efficiency of the detector. A similar spectral shape, but without $\Sigma_{\text{coh}}(\lambda)$, was used by Hubbard, Quicksall & Jacobson (1972). The function $\sum[(I_o - I_c)/\sigma]^2$ was minimized, where I_o is the observed intensity, I_c is calculated according to (4), and σ is the statistical standard deviation of the experimental values. The minimization was carried out by the computer program *FUMILI* from the program library of the JINR Computer Centre. The analyses of the 120 neutron spectrum points, measured on V within a range of wavelengths from 0.95 to 3.4 Å, allowed evaluation of the parameters C_1 to C_4 and determination of C_5 . In

* The first-order polynomial is practically always a satisfactory approximation for the background.

this case $R_w(I) = \{\sum [(I_o - I_c)/\sigma]^2 / \sum (I_o/\sigma)^2\}^{1/2}$ was 0.015, whereas the non-statistical point dispersion did not exceed 1% on average. Despite the good quality of the description of the V spectrum, this experiment did not allow a final conclusion about the values of the parameters C_1 to C_4 to be made because of the impossibility of taking the background into account exactly, the influence of multiple scattering, and the low intensity of the long-wavelength part of the spectrum. More reliable values of the function parameters (4) were found from diffraction measurements on polycrystalline Mo. The integrated intensities of the diffraction maxima are described by the formula:

$$I_{hkl} = \Phi(\lambda)\lambda^4(jF^2)_{hkl}A(\lambda), \quad (5)$$

where j is the multiplicity factor and $A(\lambda)$ is the absorption factor. The two measurements were performed (24 h each) at scattering angles of 90 and 146°, with 38 points processed. In Fig. 2, a solid line shows the effective spectrum, computed according to (4) at $C_1 = 1.7$ Å, $C_2 = 4.5$ Å, $C_3 = 0.54$ Å⁻¹, $C_4 = 0.24$ Å⁻¹, $C_5 = 32$ mm; the points indicate the values of $\Phi(\lambda)$ obtained from an experiment with Mo. The final $R_w(I)$ factor is 0.04. Let us evaluate the non-statistical contribution from the dispersion of the experimental points. The value of the structure factor of Mo divided by the scattering amplitude and the thermal factor is equal to the number of atoms in the unit cell, $F_c = 2$. The mean experimental value is:

$$\bar{F}_o = (\sum F_o/\sigma^2) / (\sum 1/\sigma^2) = 2.002 \pm 0.030. \quad (6)$$

It can be seen that non-statistical deviations scarcely contribute to the mean value. Their contribution to separate points, similar to the V experiment, does not exceed 1%.

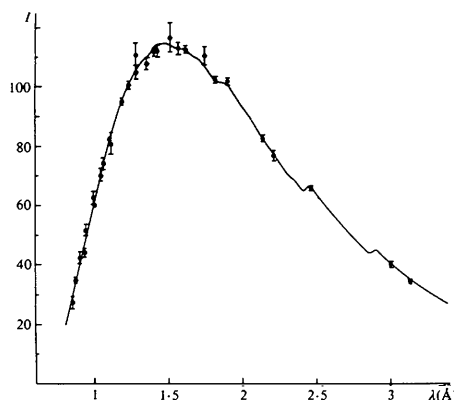


Fig. 2. An effective neutron spectrum. The solid line was calculated according to formula (4); the points are from the experiment with Mo.

5. Structure factors of perdeuterionaphthalene

The selection of perdeuterionaphthalene, $C_{10}D_8$, for the test experiment was made for two reasons. Owing to a large crystal volume the crystal gives adequately large reflection intensities, with moderate corrections for extinction since structure factors of perdeuterionaphthalene are small on average. A detailed neutron diffraction investigation has been carried out by Pawley & Yeats (1969), with $R(F) = 0.051$ for 331 reflections, *i.e.* the structure of $C_{10}D_8$ is well known. (Space group $P2_1/a$, $a = 8.266$, $b = 5.968$, $c = 8.669$ Å, $\beta = 122.92^\circ$.)

In analysing the experimental results, the diffraction maximum intensities are described by the formula:

$$I_{hkl} = \Phi(\lambda)\lambda^4 F_{hkl}^2 A(\lambda) Y(\lambda), \quad (7)$$

where $Y(\lambda)$ is the correction for extinction. The large mosaic spread ($\sim 30'$) suggests the applicability of a type I extinction model and use was hence made of the Zachariasen (1967) approximation for the calculation of $Y(\lambda)$:

$$Y(\lambda) = \left(1 + 2g \frac{\lambda^3 F_{hkl}^2}{V_c^2 \sin 2\theta} \bar{T} \right)^{-1/2}, \quad (8)$$

where g is the adjustable parameter, \bar{T} is the neutron mean path in the sample, V_c is the volume of the unit cell, and θ is the Bragg angle.

The function $\sum [(I_o - I_c)/\sigma]^2$ was minimized, with mean-square standard deviations put equal to $\sigma^2 = \sigma_I^2 + \delta^2 I^2$, where σ_I is the mean-square standard deviation from the statistics, and δ varies from 0.02 through 0.05. To compute the effective spectrum, the parameters used were taken from the experiment with Mo. In the last iterations, the quantity g and the parameters C_3 and C_4 were refined. The structure factors were computed using the coordinates of $\bar{1}$ symmetry from Pawley & Yeats (1969); neither their positional nor their thermal parameters for $C_{10}D_8$ have been varied. The data giving the progress in analysis of the 45 maxima obtained from the spherical sample with diameter 12 mm are listed in Table 1. The experimental

Table 1. Agreement indices at various stages in processing data from $C_{10}D_8$

$R(I)$ and $R(F)$ are the conventional R factors for intensity and structure factors. The final values of g , C_3 and C_4 are listed for every step, and have errors of 10.0, 0.05 and 0.05 respectively.

| | $R(I)$ | $R(F)$ | g | C_3 | C_4 |
|----|--------|--------|-----|-------|-------|
| 1* | 0.113 | 0.089 | 64 | 0.54 | 0.24 |
| 2 | 0.101 | 0.081 | 88 | 0.54 | 0.24 |
| 3† | 0.070 | 0.060 | 74 | 0.64 | 0.26 |

* Normalizing parameters only refined.

† Refinement of C_3 and C_4 included.

Table 2. Measured and calculated TOF intensities and extinction from coefficients for $C_{10}D_8$

| $h k l$ | I_o | I_c | $\sigma(I_o)$ | Y |
|---------|-------|-------|---------------|------|
| 0 0 3 | 44958 | 45156 | 926 | 0.58 |
| 0 0 4 | 76134 | 83906 | 1549 | 0.74 |
| 0 0 5 | 9125 | 7354 | 219 | 0.99 |
| 0 0 7 | 5264 | 3787 | 184 | 1.00 |
| 0 0 9 | 906 | 580 | 83 | 1.00 |
| 0 0 10 | 691 | 366 | 101 | 1.00 |
| 0 2 2 | 12187 | 12181 | 270 | 0.72 |
| 0 3 3 | 7964 | 8059 | 195 | 0.95 |
| 0 4 4 | 10941 | 10282 | 252 | 0.97 |
| 0 5 5 | 1326 | 1315 | 91 | 1.00 |

and computed intensities, statistical errors of the experimental points and the extinction coefficients for ten of the twelve crystallographic planes investigated are listed in Table 2.

A comparison between experimental and computed intensities and structure factors for $C_{10}D_8$, as well as the low values of the final R factors, shows that the method described enables values of the experimental structure factors to be obtained with the TOF-diffractometer having an average accuracy better than 10%.

6. Neutron diffraction refinement of deuterated lanthanum magnesium nitrate

The structure of the cerium magnesium nitrate [$Ce_2Mg_2(NO_3)_{12} \cdot 24H_2O$] (CMN) isomorphous with the structure of LMN, was previously studied by the X-ray method. A comparison between the experimental intensities of the diffraction peaks obtained by us and those calculated on the basis of data taken from Zalkin, Forrester & Templeton (1963), using scattering amplitudes for b_{La} instead of b_{Ce} , and b_D instead of b_H , revealed a considerable discrepancy.

This may be due to the substitution of Ce by La, the shift of the centre of gravity of the charge cloud relative to the nucleus, the isotopic effect and the reduced accuracy of the X-ray determination of the positions of the H atoms. A detailed study of similar structures [*e.g.* $(COOH)_2 \cdot 2H_2O$ and $(COOD)_2 \cdot 2D_2O$ (Coppens, Sabine, Delaplane & Ibers, 1969)] using both X-ray and neutron diffraction techniques has shown that the discrepancy between X-ray and neutron data is mainly caused by the difference in light-atom coordinates (*i.e.* H and D). Therefore, in this paper only the positional and thermal parameters of the D atoms in LMN were refined.

The sample was a plate $5 \times 25 \times 25$ mm. The c axis of the hexagonal unit cell was perpendicular to the 25×25 mm surface of the plate. The sample was deuterated to 99.3% and contained a 1% admixture of Nd. The unit-cell parameters of hexagonal LMN were determined using the Syntex $P1$ X-ray automatic diffrac-

tometer: $a = 11.041 \pm 0.005$, $c = 34.610 \pm 0.015$ Å; these are close to the corresponding cell parameters of CMN. [$a = 11.004 \pm 0.006$, $c = 34.592 \pm 0.012$ Å (Zalkin, Forrester & Templeton, 1963).]

All measurements were performed at a scattering angle of 90° . The spectrum from (001) measured in 2 h is shown in Fig. 3. The higher-order reflections from 38 crystal planes were observed in about 50 h, giving about 200 independent reflections. 164 reflections had intensities higher than three standard deviations. The experimental data were treated as in the case of perdeuteronaphthalene, but with the C_3 parameter fixed. A neutron wavelength-dependent linear absorption coefficient was calculated from the known incoherent and absorption cross section of the LMN atoms as $(0.096 + 0.018\lambda)$ cm^{-1} . The absorption factor was given by

$$A(\lambda) = \frac{1}{V} \int \exp[-\mu(\lambda) \cdot t] dV,$$

where V is the whole crystal volume and t is the total path length of the neutron beam in the crystal. The absorption correction did not exceed 20%. Nuclear scattering amplitudes of all atoms in LMN were taken from Bacon (1972). Together with Φ_0 and C_4 , g , the position coordinates, and the isotropic thermal factors of the eight D atoms were taken as variable. During the initial iterations the parameters Φ_0 , C_4 and g only were varied. This led to $R(I) = \sum |I_o - I_c| / \sum I_o = 0.42$ for $C_4 = 0.024$ Å $^{-1}$ and $g = 3 \times 10^3$. When all the coordinates and thermal factors of the D atoms were varied, the $R(I)$ value decreased to 0.14. Table 3 gives the refined relative coordinates and thermal parameters of the D atoms, using the same notation as Zalkin, Forrester & Templeton (1963). The estimation of error in the coordinates took the dependence of the final results on the initial set of parameters into account. The errors for x and y coordinates do not exceed 0.003 relative units, and z coordinates do not exceed 0.001, which is ~ 0.03 Å for the three axes together. The observed reflection data are listed in Table 4.* A

* Table 4 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33769 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

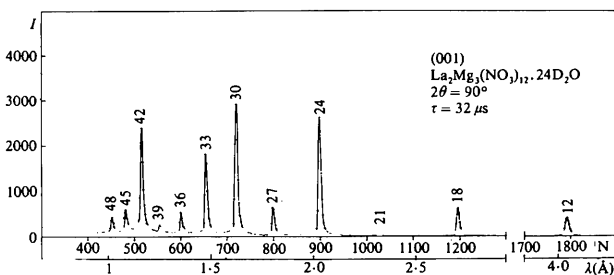


Fig. 3. A typical neutron diffraction spectrum.

comparison of the bond lengths and angles is given in Tables 5 and 6, from which it follows that all the O—P distances are lengthened and the $P \cdots O$ distances shortened, on average by about 0.2 Å. Angles between the O—P and $P \cdots O$ vectors increased between 7 and 18° , thus approaching the value 180° . P stands for H in the case of X-ray and for D in the case of neutron coordinates. The systematic character of the changes in bond lengths and angles means that they are not due to random deviations in the X-ray coordinates of the H atoms but are due to systematic deviations from the corresponding neutron coordinates of the D atoms, in agreement with the known shift of the electron shell of H or D toward the atom to which it is bound. The deviations in H positional parameters determined by X-ray diffraction, and estimated by Zalkin, Forrester & Templeton (1963) as 0.2 Å, seem to be exceeded only for the positions of H(1W2) and H(2W4). The X-ray data for H(1W2) give a value that is too small for the O—H bond distance and an O—H \cdots O angle that differs appreciably from the neutron value. The position

Table 3. Relative coordinates and isotropic thermal parameters of the deuterium atoms in $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{D}_2\text{O}$

Standard deviations are: $\sigma(x) = \sigma(y) = 0.003$, $\sigma(z) = 0.001$.

| | x | y | z | B (Å 2) |
|--------|--------|--------|-------|---------------|
| D(1W1) | 0.070 | 0.190 | 0.058 | 2.6 |
| D(2W1) | -0.007 | 0.226 | 0.022 | 4.1 |
| D(1W2) | 0.170 | 0.050 | 0.370 | 2.5 |
| D(2W2) | 0.167 | -0.068 | 0.393 | 1.2 |
| D(1W3) | 0.253 | 0.199 | 0.452 | 1.5 |
| D(2W3) | 0.152 | 0.213 | 0.477 | 5.3 |
| D(1W4) | 0.235 | 0.195 | 0.107 | 3.1 |
| D(2W4) | 0.121 | 0.195 | 0.130 | 3.0 |

Table 5. A comparison of some interatomic distances (Å) obtained by neutron and X-ray techniques

For neutron distances the standard deviations are given in parentheses and correspond to the least significant digit.

| | Neutron | X-ray | Difference |
|-------------------------|----------|-------|------------|
| O(W1)—P(1W1) | 0.97 (3) | 0.75 | 0.22 |
| O(W1)—P(2W1) | 0.99 (4) | 0.71 | 0.28 |
| O(W2)—P(1W2) | 0.87 (3) | 0.53 | 0.34 |
| O(W2)—P(2W2) | 0.97 (4) | 0.81 | 0.16 |
| O(W3)—P(1W3) | 0.97 (3) | 0.76 | 0.21 |
| O(W3)—P(2W3) | 0.88 (4) | 0.63 | 0.26 |
| O(W4)—P(1W4) | 0.98 (4) | 0.87 | 0.11 |
| O(W4)—P(2W4) | 1.00 (3) | 0.82 | 0.18 |
| P(1W1) \cdots O(W4) | 1.86 (3) | 2.11 | -0.25 |
| P(2W1) \cdots O(N12)' | 2.02 (4) | 2.31 | -0.29 |
| P(1W2) \cdots O(N11)' | 2.13 (4) | 2.50 | -0.37 |
| P(2W2) \cdots O(N13)' | 1.81 (4) | 1.98 | -0.17 |
| P(1W3) \cdots O(W4)' | 1.85 (3) | 2.06 | -0.21 |
| P(1W4) \cdots O(N23)' | 1.93 (4) | 2.13 | -0.20 |
| P(2W4) \cdots O(N21)' | 2.16 (4) | 2.40 | -0.24 |
| P(2W4) \cdots O(N22)' | 2.41 (4) | 2.41 | -0.00 |

Table 6. A comparison of some valence angles ($^{\circ}$)
— obtained by neutron and X-ray techniques

For neutron angles the standard deviations are given in parentheses.

| | Neutron | X-ray |
|--------------------------|---------|-------|
| O(W1)—P(1W1) ... O(W4) | 173 (3) | 158 |
| O(W1)—P(2W1) ... O(N12)' | 164 (3) | 157 |
| O(W2)—P(1W2) ... O(N11)' | 160 (3) | 146 |
| O(W2)—P(2W2) ... O(N13)' | 177 (2) | 168 |
| O(W3)—P(1W3) ... O(N4)' | 175 (3) | 168 |
| O(W4)—P(1W4) ... O(N23)' | 162 (3) | 144 |
| O(W4)—P(2W4) ... O(N21) | 153 (2) | 142 |
| O(W4)—P(2W4) ... O(N22)' | 114 (3) | 127 |

of H(2W4) was interpreted by Zalkin, Forrester & Templeton (1963) as resulting from a bifurcated hydrogen bond between O(W4) and O(N21) and O(N22). However, the neutron data show that the symmetry between O(N21) and O(N22) with respect to O(W4)—H(2W4) is substantially destroyed (Fig. 4): there is hence only a conventional weak hydrogen bond between O(W4) and O(N21).

7. Conclusions

The results of the present paper confirm the conclusion made earlier by Buras *et al.* (1965) and Day & Sinclair (1970) that time-of-flight diffractometers allow structure determinations of single crystals to be made even with a weak pulsed neutron source. It now appears possible to start systematic investigations of complex and biological compounds on the basis of a number of new powerful pulsed sources which are planned or built.

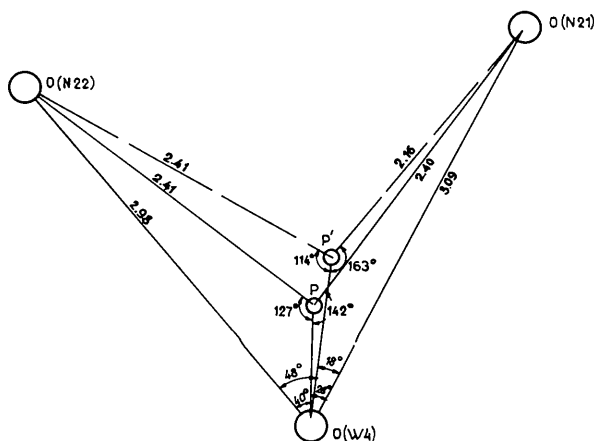


Fig. 4. The environment of the P(2W4) atom. The position P corresponds to the X-ray coordinates of the H atom, P' to the neutron coordinates of the D atom. The distances are given in Å.

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