

## The Crystal and Molecular Structure of Pyridine Picrate

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Optical transform methods have been used to determine the approximate structure of pyridine picrate ( $C_5H_5N \cdot C_6H_3N_3O_7$ ) from two-dimensional X-ray intensity data. The space group is  $P2_1/c$  with four molecules in the unit cell of dimensions  $a = 12.15$ ,  $b = 3.78$ ,  $c = 26.60$  Å and  $\beta = 93^\circ$ . The structure was refined by Fourier, difference Fourier and least-squares methods. The H atoms were revealed in the final difference Fourier synthesis. The acid-base pairs of the charge-transfer complex are held together in the ground state by hydrogen bonds to form an infinite chain around the twofold screw axis parallel to  $b$ .

### Introduction

Pyridine picrate ( $C_5H_5N \cdot C_6H_3N_3O_7$ ) belongs to the well known group of complexes in which polynitroaromatic substances combine with aromatic hydrocarbons, bases and their derivatives through charge-transfer interactions in a 1:1 molar ratio to form crystalline molecular addition compounds. X-ray diffraction studies of these charge-transfer complexes are considered important for the understanding of their structures and the nature of bonds involved. Our interest in the problem, however, arose from a different consideration. The complex comprising the electron donor pyridine and the electron acceptor picric acid (Fig. 1) is composed of atoms having nearly similar scattering power and with structural groups in the form of ring configurations that usually display significant features in the transform space. Moreover, the unit-cell dimensions are favourable for a structural study in projection. The problem is thus well suited for investigation by optical-transform methods (Hanson, Lipson & Taylor, 1953). Though a three-dimensional analysis is essential for the precise examination of the bonding, the ease with which the structure is revealed from two-dimensional data is considered worth reporting.

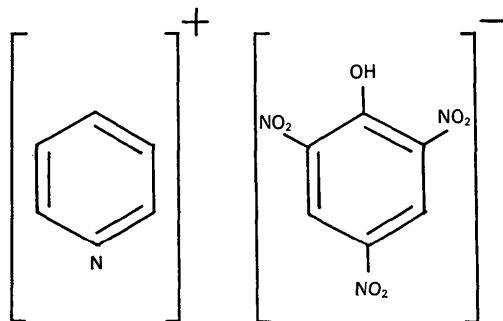


Fig. 1. Molecule of pyridine picrate.

### Experimental

The crystals of pyridine picrate were obtained in the form of soft yellowish laths, elongated along the  $b$  axis, by recrystallization from solution in alcohol. Unit-cell dimensions were measured from rotation, oscillation and Weissenberg photographs calibrated with Si ( $a = 5.4305$  Å) powder lines. The space group  $P2_1/c$  was indicated by systematic absences  $h0l$ ,  $l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$ . The density was measured by flotation in a mixture of carbon tetrachloride and bromoform. The crystal data are listed in Table 1.

Table 1. Crystal data

Molecular formula	$C_{11}H_8N_4O_7$
M.W.	308.1
m.p.	167°C
Space group	$P2_1/c$ (monoclinic)
$a = 12.15$ (2) Å	$D_m = 1.62$ g cm $^{-3}$
$b = 3.78$ (1)	$D_c = 1.67$ for $Z = 4$
$c = 26.60$ (2)	$\mu = 11.5$ cm $^{-1}$ for
$\beta = 93^\circ$	Cu $K\alpha = 1.5405$ Å
$V = 1219.95$ Å $^3$	$F(000) = 632$

Unfiltered Cu  $K\alpha$  radiation was used to record  $h0l$  and  $0kl$  reflexions on zero-layer Weissenberg photographs with the multiple-film technique. Intensities were measured by visual comparison with calibrated diffraction spots of known relative exposures obtained from the same crystal, and were corrected for Lorentz-polarization. No absorption correction was considered necessary. A Wilson plot was made to place the intensities on an approximate absolute scale and gave a mean isotropic temperature factor  $B = 3$  Å $^2$ .

### Structure determination and refinement

The space group  $P2_1/c$  projects onto (010) as plane group  $P2$  and the effective unit cell of projection contains only two centrosymmetrically related molecules.

Thus for the optical-transform test of molecular shape in projection the transform of a single molecule should be considered (Chaudhuri, 1972). The  $h0l$  section of the weighted reciprocal lattice [Fig. 2(a)] clearly reveals the characteristic benzene transform consisting of six clusters of strong reflexions lying more or less close to the benzene circle. This suggests that the pyridine ring and the phenyl ring of picric acid have approximately parallel orientation in the (010) projection. Fig. 2(b) shows the derivation of the shape and orientation of the rings from the benzene peaks. Assuming normal bond lengths and bond angles a molecular model in projection is immediately arrived at by linking the two

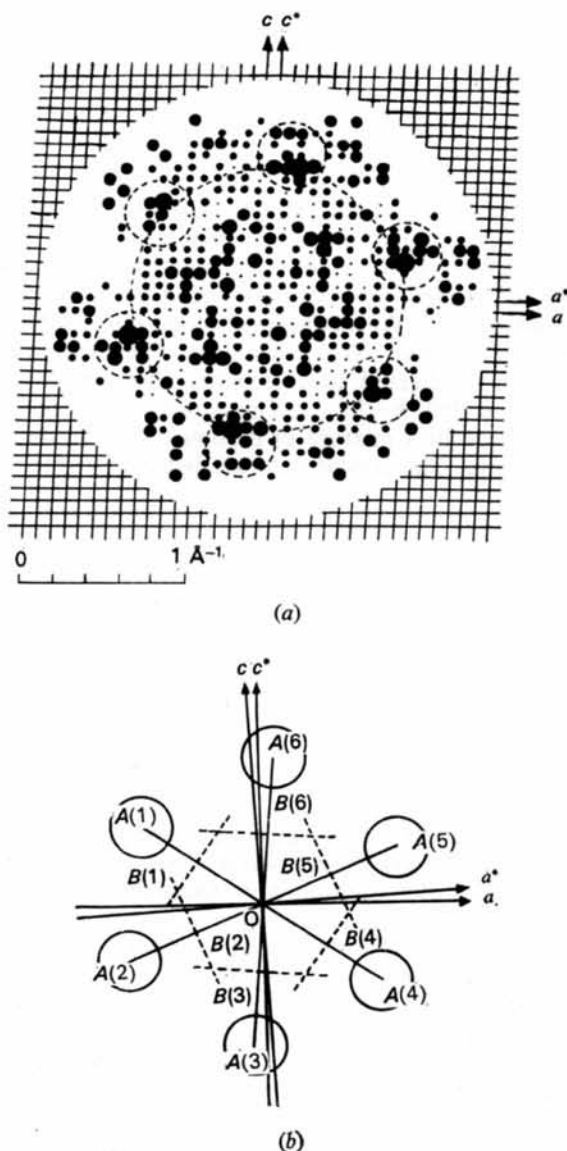


Fig. 2. (a)  $h0l$  section of the weighted reciprocal lattice of pyridine picrate with weights proportional to approximate unitary structure factors. (b) Derivation of shape and orientation of the ring structure from the benzene transform.

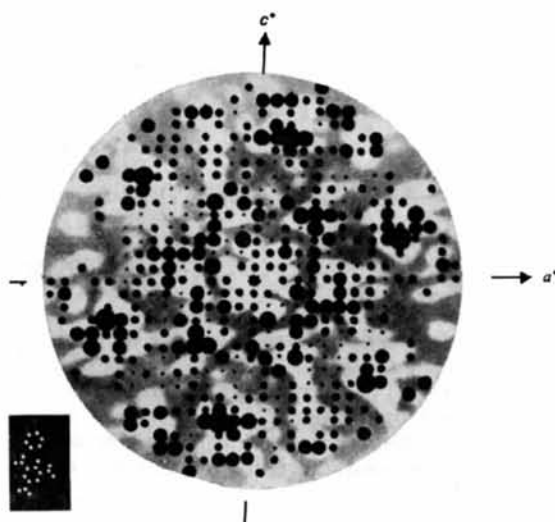


Fig. 3. Optical-transform agreement of the projection of a single molecule of pyridine picrate derived optically.

components of the complex through a hydrogen bond between the N atom of pyridine and the hydroxylic O of picric acid. The model was refined optically as far as possible and the agreement for the optically refined model is shown in Fig. 3.

The molecular structure-factor graphs (Taylor & Morley, 1959) were drawn to determine the relative positions of the molecules in the unit cell. These are contour graphs indicating variation in the contribution to the structure factor of one reflexion due to variation in position of a molecule and its plane-group related counterparts in the unit cell. The total contribution of the four molecules of pyridine picrate in the unit cell to the structure factor of the reflexion  $h0l$  is given by

$$G(h0l) = 4 \cos 2\pi(hX + lZ) [A(h0l) - B(h0l)] - 4 \sin 2\pi(hX + lZ) [C(h0l) - D(h0l)]$$

where

$$A(h0l) = \sum_n f_n \cos 2\pi h x_n \cos 2\pi l z_n$$

$$B(h0l) = \sum_n f_n \sin 2\pi h x_n \sin 2\pi l z_n$$

$$C(h0l) = \sum_n f_n \cos 2\pi h x_n \sin 2\pi l z_n$$

$$D(h0l) = \sum_n f_n \sin 2\pi h x_n \cos 2\pi l z_n$$

Here  $x_n$  and  $z_n$  are the fractional parameters of the  $n$ th atom with respect to an arbitrarily chosen origin in the molecule while  $X$  and  $Z$  are the parameters of this origin with respect to the true origin in the unit cell (Fig. 4). The combined molecular structure-factor graphs are drawn (Fig. 5) summing up the computed values of  $G(h0l)$  in the essential ranges of  $X$  and  $Z$  for six reflexions (100, 202, 0,0,24, 10,0,10, 3,0,24 and 904) having zero observed  $F(h0l)$  values. The position ( $X=0.235$ ,  $Z=0.165$ ) of the arbitrary origin with respect to the true origin is given by the lowest contour of the function. The accuracy of the molecular location is immediately ensured by the optical-transform test with two centrosymmetrically related molecules, as shown in Fig. 6.

The first  $F_o(h0l)$  synthesis computed with 185 reflexions (out of 241 experimentally observed  $h0l$  reflexions), the phases of which were quickly derived optically (Lipson & Taylor, 1951), revealed the complete molecule. The structure was then refined by successive Fourier syntheses. The electron-density projection on (010) computed with all the observed structure factors is shown in Fig. 7. The agreement residual  $R = \sum[|F_o| - |F_c|] / \sum|F_o|$  calculated at this stage, using the same isotropic temperature factor  $B = 4.0 \text{ \AA}^2$  was 23%.

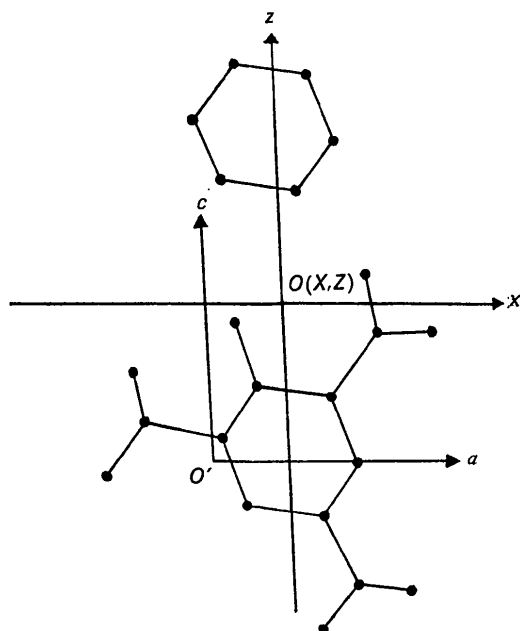


Fig. 4. The relationship between the coordinates of the atoms of the trial molecular model of pyridine picrate with respect to the arbitrary origin ( $O$ ) and with respect to the true origin ( $O'$ ) of the unit cell.

Four cycles of refinement by  $(F_o - F_c)$  synthesis reduced  $R$  to 18%. The atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were adopted for all structure factor calculations. Corrections for secondary extinction were considered necessary for a few low-angle reflexions ( $\bar{1}06$ ,  $204$  and  $302$ ) for which the calculated structure factors were found to be consistently higher than the observed values. An extinction correction for these reflexions by an empirical method suggested by Pinnock, Taylor & Lipson (1956) reduced  $R$  to 16%. The atomic coordinates and the individual isotropic temperature factors for the non-hydrogen atoms were further refined by least-squares calculations on an IBM 1620 computer at the Indian Institute of Technology, Kharagpur (West Bengal, India) using the *SFLS* program of G. A. Mair (Pure Chemistry Division, National Research Council, Ottawa, Canada). The function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The weighting function was of the form

$$w = \frac{1}{1 + \left(\frac{KF_o - b}{a}\right)^2}$$

where  $a = 8F_{\min}$  and  $b = 5F_{\min}$ . Two cycles of least-squares refinement reduced  $R$  to 12%. An  $(F_o - F_c)$  synthesis computed at this stage revealed the positions of the H atoms with peak heights ranging from 0.25 to 0.37  $e \text{ \AA}^{-2}$  (Fig. 8). The hydroxylic H of picric acid did not appear at the expected site. However the appearance of a peak of 0.29  $e \text{ \AA}^{-2}$  near O(4) of the nitro group might suggest a tautomeric shift of the hydroxylic H to the nitro group. The inclusion of the H atom parameters in the structure-factor calculation reduced  $R$  to 11%. The H atoms were assigned the same temperature factors as the atoms to which they are bonded.

The solution of the (100) projection was straightforward. An approximate model of the molecular shape

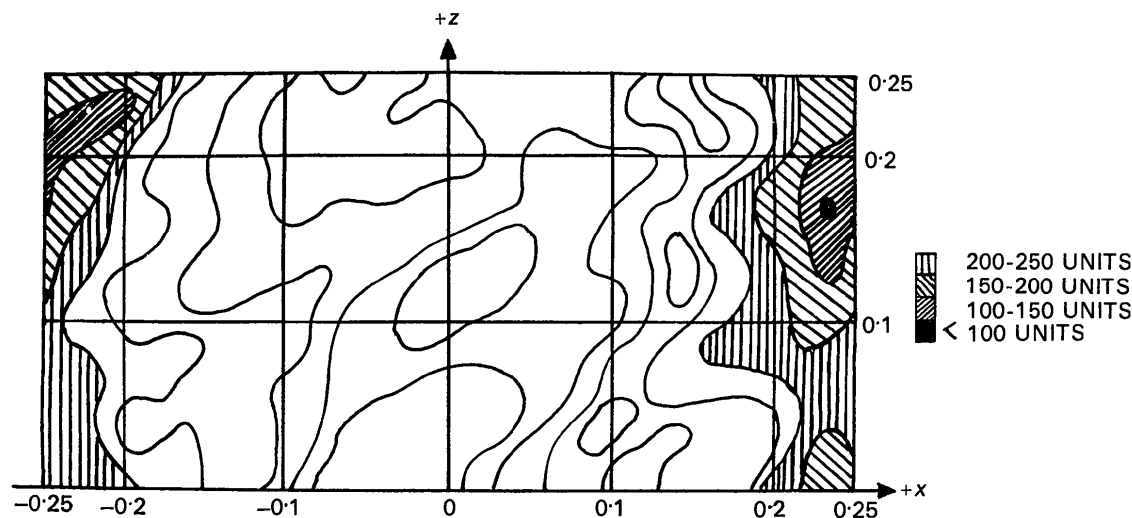


Fig. 5. The combined molecular structure-factor graph for six reflexions of pyridine picrate.

was obtained by projecting optically onto (100) a wire model of the molecule which was oriented so that its shadow fitted fairly well with the electron-density projection on (010). Packing considerations supported by the optical transform test indicated an approximate structure comprising the four molecules in projection related by the symmetry of plane group  $pgg$ . The model which gave an agreement residual of 36% was refined by  $F_o$  and  $(F_o - F_c)$  syntheses to an  $R$  value of 21%.

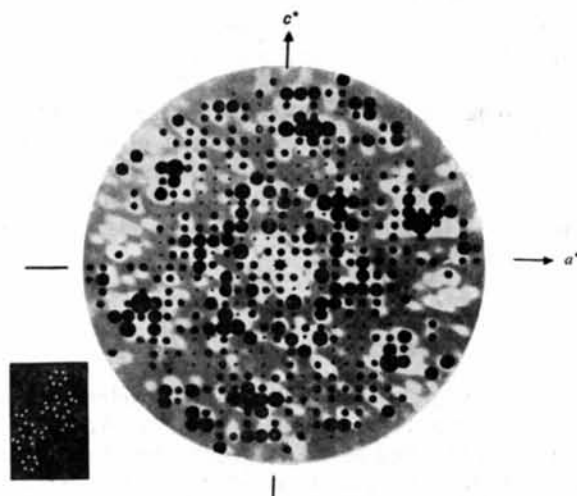


Fig. 6. Optical-transform agreement of the approximate structure of two centrosymmetrically related molecules of pyridine picrate in the unit cell of projection.

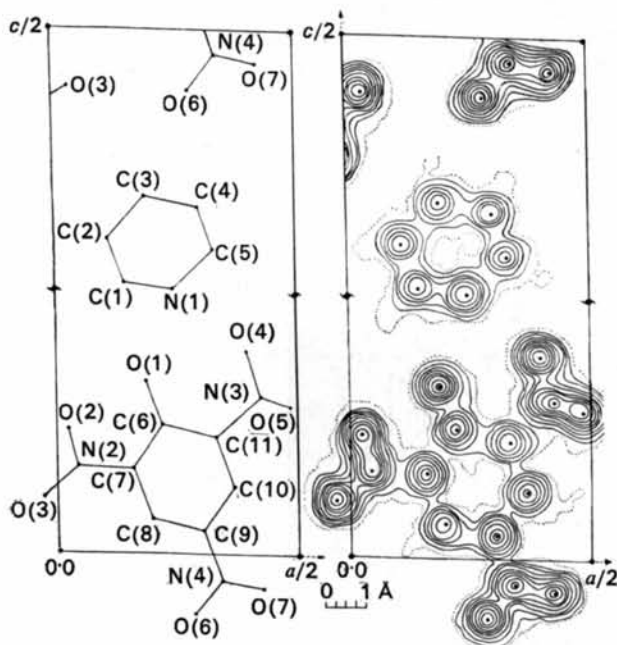


Fig. 7. Electron density projection on (010). Contours are drawn at intervals of  $0.5 \text{ e } \text{Å}^{-2}$ . The  $0.5 \text{ e } \text{Å}^{-2}$  contour is dotted. The atomic positions are indicated in the diagram shown alongside.

The final electron density projection along [100] shows a considerable amount of overlap (Fig. 9) resulting in poor resolution of the atoms in the projected structures. As objective determination of the H atom positions was not possible in this projection the  $y$  coordinates were calculated using their  $x$  and  $z$  coordinates from the (010) projection and assuming C-H and O-H bond distances of 1.09 and 0.90 Å respectively. The inclusion of these calculated H atom parameters reduced  $R$  to 20%.

Table 2 lists the final atomic coordinates with their isotropic temperature factors.\*

Table 2. Final atomic coordinates

	$X(\text{Å})$	$Y(\text{Å})$	$Z(\text{Å})$	$B(\text{Å}^2)$
C(1)	1.73	-1.82	6.94	4.9
C(2)	1.32	-1.25	8.08	4.4
C(3)	2.34	-1.05	9.08	5.1
C(4)	3.58	-1.65	8.96	4.3
C(5)	3.94	-2.20	7.74	5.0
C(6)	2.68	-1.08	3.27	3.5
C(7)	1.88	-1.12	2.12	3.2
C(8)	2.29	-0.80	0.82	3.6
C(9)	3.59	-0.45	0.61	3.2
C(10)	4.44	-0.55	1.79	3.1
C(11)	4.00	-0.85	3.00	3.5
N(1)	2.98	-2.30	6.77	4.6
N(2)	0.51	-1.60	2.23	3.7
N(3)	5.03	-0.50	4.11	3.8
N(4)	4.10	0.25	-0.65	3.7
O(1)	2.25	-0.82	4.44	3.7
O(2)	0.28	-2.28	3.13	4.6
O(3)	-0.34	-1.62	1.34	4.3
O(4)	4.78	-1.15	5.22	4.7
O(5)	5.79	0.50	3.83	4.5
O(6)	3.38	-0.25	-1.61	4.9
O(7)	5.06	1.05	-0.85	4.8
H(1)	0.87	-1.57	6.25	4.9
H(2)	0.43	-0.63	7.98	4.4
H(3)	2.18	-0.28	9.84	5.1
H(4)	4.09	-1.25	9.55	4.3
H(5)	4.70	-2.69	7.13	5.0
H(6)	1.63	-1.10	-0.10	3.6
H(7)	5.25	-0.13	1.44	3.1
H(8)	4.25	-1.82	5.50	4.7

The average standard deviations in the atomic coordinates as estimated according to the formula of Cruickshank (1960) are as follows:  $\sigma(X) = 0.015$ ,  $\sigma(Y) = 0.060$ ,  $\sigma(Z) = 0.015$ .

In view of the poor resolution of the atoms in the (100) projection, the average standard deviation of  $y$  is definitely an underestimation. The crystal structure of pyridine picrate as viewed along  $b$  is depicted in Fig. 10 where the intermolecular contact distances are also indicated. The covalent bond lengths and bond angles are given in Table 3. The errors in the bond lengths indicated in parentheses are standard deviations.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31284 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

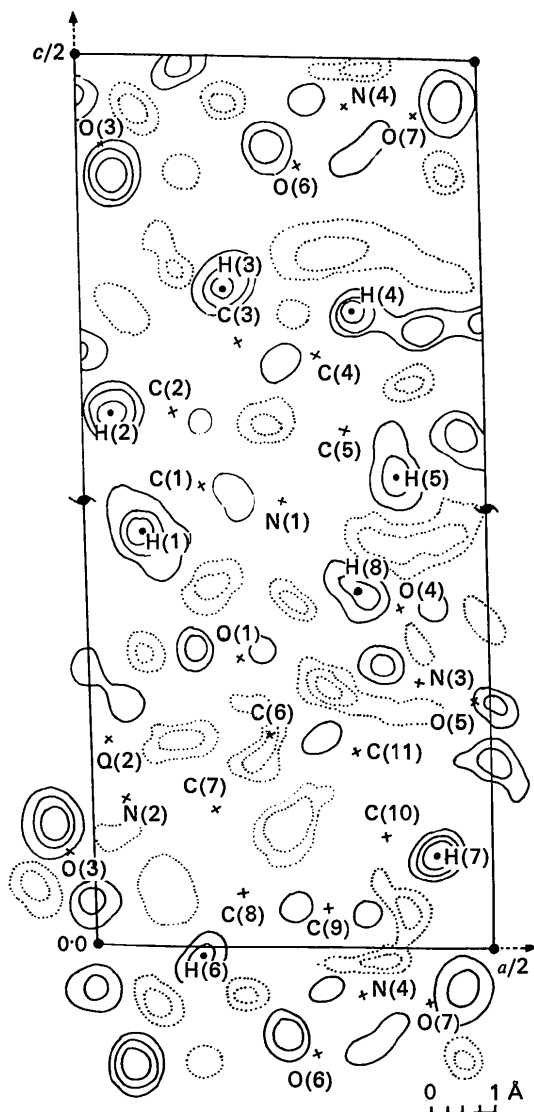


Fig. 8. ( $F_o - F_c$ ) synthesis projected on (010). The proposed H atom positions are indicated by •.

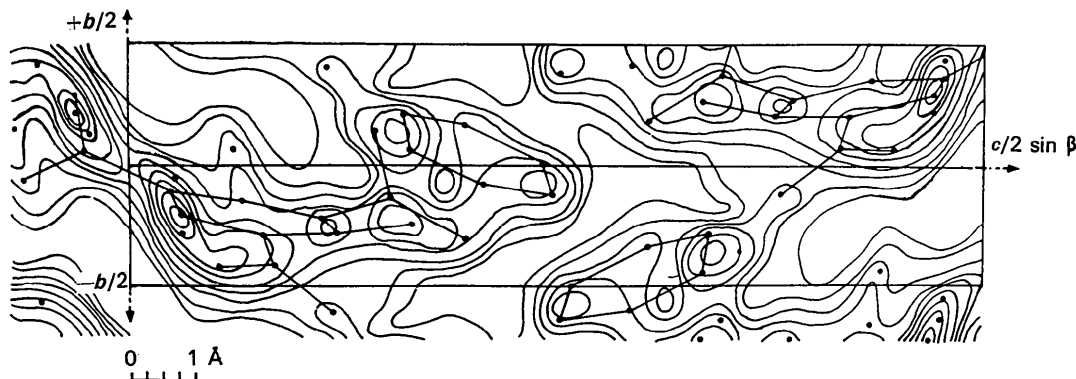


Fig. 9. Electron-density projection on (100). Contours are drawn at intervals of  $0.5 e \text{ \AA}^{-2}$ .

tions estimated using the formula given by Ahmed & Cruickshank (1963). Although a high degree of accuracy is not claimed the bond lengths and bond angles on average satisfy the requirements of a normal valency structure. The nitro groups appear to be slightly distorted. This may be due to local molecular overcrowding.

Table 3. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

C(1)—C(2)	1.35 (5)	C(1)—C(2)—C(3)	115.4
C(2)—C(3)	1.41 (2)	C(2)—C(3)—C(4)	120.3
C(3)—C(4)	1.39 (4)	C(3)—C(4)—C(5)	120.6
C(4)—C(5)	1.40 (3)	C(4)—C(5)—N(1)	117.3
C(5)—N(1)	1.33 (2)	C(5)—N(1)—C(1)	121.1
N(1)—C(1)	1.35 (3)	N(1)—C(1)—C(2)	125.0
C(6)—C(7)	1.37 (2)	C(6)—C(7)—C(8)	125.9
C(7)—C(8)	1.42 (2)	C(7)—C(8)—C(9)	121.7
C(8)—C(9)	1.37 (3)	C(8)—C(9)—C(10)	113.7
C(9)—C(10)	1.42 (2)	C(9)—C(10)—C(11)	121.7
C(10)—C(11)	1.34 (2)	C(10)—C(11)—C(6)	124.8
C(11)—C(6)	1.38 (2)	C(11)—C(6)—C(7)	111.4
C(7)—N(2)	1.46 (3)	C(7)—C(6)—O(1)	124.2
C(11)—N(3)	1.51 (2)	C(11)—C(6)—O(1)	124.1
C(9)—N(4)	1.54 (4)	N(2)—C(7)—C(6)	117.2
C(6)—O(1)	1.29 (2)	N(2)—C(7)—C(8)	117.4
N(2)—O(2)	1.16 (4)	O(2)—N(2)—C(7)	118.2
N(2)—O(3)	1.20 (2)	O(3)—N(2)—C(7)	125.2
N(3)—O(4)	1.30 (4)	O(2)—N(2)—O(3)	114.4
N(3)—O(5)	1.29 (4)	O(4)—N(3)—C(11)	112.1
N(4)—O(6)	1.27 (3)	O(5)—N(3)—C(11)	113.7
N(4)—O(7)	1.27 (5)	O(5)—N(3)—O(4)	133.7
		C(10)—C(11)—N(3)	112.0
		C(6)—C(11)—N(3)	121.2
		C(9)—N(4)—O(7)	131.4
		C(9)—N(4)—O(6)	105.0
		O(6)—N(4)—O(7)	122.2
		C(8)—C(9)—N(4)	126.9
		C(10)—C(9)—N(4)	118.0

The equations through the least-squares planes are: for the phenyl ring of picric acid

$$0.176x - 0.949y - 0.167z = 1$$

pyridine ring

$$-0.087x - 0.246y + 0.101z = 1$$

O(2)—N(2)—O(3) nitro group

$$0.690x - 1.421y - 0.812z = 1$$

