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The Structure of *p*-Nitrotoluene*

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Crystals of *p*-nitrotoluene, $CH_3C_6H_4NO_2$, are orthorhombic, space group *Pcab*, with $a=6{\cdot}43$, $b=14{\cdot}07$, $c=15{\cdot}66$ Å^2; ϱ_o, 1·294 g.cm^{-3}; ϱ_c for $Z=8$, 1·287 g.cm^{-3}. The structure was refined by the method of least squares to an R value of 0·107 for 467 observed reflexions. The molecular dimensions are compared with those of related molecules. The nitro group has pronounced torsional oscillation; as in *p*-toluic acid, the methyl group is vibrating normal to the C–C bond.

Experimental

The pale yellow needle-like crystals grown from aqueous alcohol are orthorhombic. The cell dimensions determined from equatorial Weissenberg photographs are $a=6{\cdot}43$, $b=14{\cdot}07$, $c=15{\cdot}66$ Å; the data reported by Prasad & Merchant (1938) are $a=6{\cdot}41$, $b=14{\cdot}10$, $c=15{\cdot}39$ Å; space group, *Pcab*. a was measured from four reflexions having θ between 46° and 76°, b from five having θ between 41° and 61° and c from four reflexions having θ between 51° and 75°; the maximum scatter from mean values was 0·01 Å for a, 0·03 Å for b and 0.02 Å for c. The observed systematic absences confirmed the space group reported by Prasad & Merchant (1938). The other crystal data are ϱ_o, 1·294 g.cm^{-3}; ϱ_c for $Z=8$, 1·287 g.cm^{-3}; μ for Cu $K\alpha$, 9·8 cm^{-1}.

The crystals sublime on exposure to the atmosphere and had to be enclosed and sealed within thin walled glass capillaries in order to use them for collecting intensity data. Data were collected with unfiltered Cu radiation from zero to fifth layer equi-inclination Weissenberg photographs about the a axis and from zero to second layer photographs about the b axis; the crystals used for the two sets of photographs had the cross sections $1{\cdot}0\times0{\cdot}8$ and $1{\cdot}0\times0{\cdot}9$ mm^2 and lengths 2 and 1 mm respectively. Of the 469 independent reflexions, 96 were present in both sets of photographs. The intensities were corrected for various factors and brought to a common scale in the usual way (Takwale & Pant, 1971).

Determination and refinement of the structure

The structure was solved in the (100) projection with the help of a (100) sharpened Patterson projection and $(\frac{1}{2},y,0)$ and $(0,\frac{1}{2},z)$ Harker lines on the basis of a plane molecule with usual bond lengths and angles; x parameters were determined with the help of the $(x,0,\frac{1}{2})$ Harker line. The structure was first refined with the help of $0kl$ and $h0l$ reflexions to an R value of about 0·3 for general reflexions using an overall temperature factor (4·6 Å^2) obtained by Wilson's method. Six cycles of least-squares refinement of atomic parameters and individual isotropic temperature factors and correction of some numerical and indexing errors reduced R to about 0·18. Further refinement was carried out with anisotropic temperature factors using the block diagonal approximation; to start with, unit weights were given to all F's and later the following weighting scheme was used:

$$w=\frac{1}{a+|F_o|+c|F_o|^2}\,,$$

where $a=2F_{\rm min}$ and $c=2/F_{\rm max}$ (Cruickshank, 1965); R at this stage was about 0·13. The atomic parameters of the hydrogen atoms of the benzene ring were ob-

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Table 1. *Final atomic and thermal parameters*

Thermal parameters ($\times 10^4$) are of the form $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2(b_{12}hk+b_{23}kl+b_{13}hl))]$. The e.s.d.'s are given in parentheses and refer to the last significant figures.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	0·1204 (8)	0·1144 (3)	−0·0232 (3)	230 (14)	41 (2)	34 (2)	7 (6)	1 (2)	−9 (5)
C(2)	−0·0817 (8)	0·1526 (3)	−0·0280 (3)	184 (14)	46 (3)	48 (3)	−6 (6)	6 (2)	−22 (6)
C(3)	−0·1899 (8)	0·1606 (4)	0·0479 (3)	198 (15)	56 (3)	54 (3)	−3 (6)	4 (3)	−8 (6)
C(4)	−0·1064 (9)	0·1338 (4)	0·1260 (3)	267 (16)	51 (3)	45 (3)	−17 (7)	−3 (2)	10 (6)
C(5)	0·0964 (10)	0·0968 (4)	0·1261 (3)	299 (18)	61 (3)	44 (3)	1 (7)	11 (3)	−30 (7)
C(6)	0·2090 (9)	0·0879 (4)	0·0513 (3)	221 (16)	55 (3)	48 (3)	0 (6)	10 (3)	−4 (6)
C(7)	−0·2272 (12)	0·1438 (5)	0·2076 (4)	480 (25)	95 (5)	55 (3)	11 (12)	−11 (4)	69 (9)
O(1)	0·4148 (7)	0·0741 (4)	−0·1004 (3)	291 (13)	126 (4)	74 (3)	42 (7)	11 (3)	40 (7)
O(2)	0·1589 (8)	0·1322 (5)	−0·1693 (3)	422 (15)	169 (5)	41 (2)	71 (8)	23 (3)	0 (5)
N	0·2420 (8)	0·1090 (3)	−0·1031 (3)	244 (12)	59 (3)	49 (2)	−12 (6)	2 (2)	16 (5)
H(1)	−0·146 (9)	0·177 (4)	−0·083 (4)						
H(2)	−0·328 (9)	0·184 (5)	0·051 (4)						
H(3)	0·133 (10)	0·073 (5)	0·177 (4)						
H(4)	0·348 (10)	0·063 (4)	0·053 (4)						
H(5)	−0·201 (11)	0·121 (5)	0·259 (4)						
H(6)	−0·258 (13)	0·185 (5)	0·228 (4)						
H(7)	−0·278 (12)	0·104 (5)	0·209 (4)						

tained from their expected positions in the molecule and were included in the structure factor calculations. For the refinement, the unobserved reflexions having a threshold value less than F_c were also used. The thermal parameters of the hydrogen atoms were assumed to be the same as those of the carbon atoms to which they are attached. Three cycles of refinement keeping hydrogen parameters fixed reduced R to 0·118. The atomic parameters of the hydrogen atoms of the methyl group were then obtained from difference Fourier syntheses. Three more cycles of refinement including all the hydrogen atoms reduced R to 0·111; during these cycles, atomic parameters of hydrogen atoms were also refined although their thermal parameters were kept constant. The reflexions with $\Delta F>5$ were then given zero weight and three more cycles of refinement were given. Final R for observed reflexions was 0·107; 002 and 040 appear to be subject to extinction and were excluded from all calculations. The final atomic and thermal parameters along with their estimated standard deviations (e.s.d.'s) are given in Table 1 and F_o and F_c in Table 2.

Table 2. *Observed and calculated structure factors*

h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c
0	0	2	61.0	107.2	0	9	6	16.3	16.4	1	4	3	41.6	-40.6	1	12	0	20.7	-24.1
0	0	4	67.0	-62.7	0	9	8	21.2	22.1	1	4	4	5.9	5.4	1	12	2	6.9	- 9.0
0	0	8	3.7	5.1	0	10	4	14.4	-13.9	1	4	5	3.4	4.1	1	12	12	3.8	6.7
0	0	10	6.6	5.4	0	10	6	9.4	- 9.4	1	4	6	22.5	24.1	1	14	4	6.4	6.3
0	0	12	24.4	-26.0	0	10	8	5.1	6.7	1	4	7	13.5	13.9	1	16	0	4.2	5.9
0	0	14	21.8	-23.0	0	11	2	9.1	7.1	1	4	8	7.3	5.4	2	0	0	68.3	-92.8
0	0	16	4.7	- 4.7	0	11	4	8.8	8.0	1	4	11	8.4	- 6.2	2	1	1	13.5	14.7
0	2	0	27.1	29.2	0	11	6	12.1	12.2	1	4	12	15.5	17.0	2	1	2	2.4	1.6
0	4	0	110.0	-283.8	0	12	2	8.6	10.2	1	4	14	6.5	7.4	2	1	3	27.3	23.1
0	6	0	21.7	-24.3	0	12	6	4.6	- 5.9	1	5	1	26.5	-27.4	2	1	4	28.2	22.3
0	8	0	33.3	37.6	0	12	8	9.6	- 8.7	1	5	2	28.5	-28.1	2	1	5	28.7	-24.3
0	12	0	6.4	6.3	0	12	10	4.7	- 6.1	1	5	3	11.3	11.0	2	1	6	63.5	54.3
0	16	0	6.7	- 6.8	0	13	4	5.1	- 5.7	1	5	4	12.1	10.8	2	1	7	15.6	-14.1
0	1	4	8.5	9.4	0	13	6	5.1	- 5.9	1	5	5	13.7	-12.8	2	1	8	7.4	5.4
0	1	6	13.0	-15.4	0	13	8	6.6	-5.9	1	5	6	19.1	18.2	2	1	9	16.1	15.5
0	1	8	13.4	13.9	0	15	2	5.5	- 6.9	1	5	7	22.2	-21.8	2	1	10	5.3	6.5
0	1	10	14.0	-14.9	0	15	4	3.8	- 4.8	1	5	8	16.7	16.4	2	1	11	7.9	- 9.1
0	1	12	24.5	30.3	1	1	1	76.6	68.0	1	5	11	9.7	9.8	2	1	14	8.7	- 5.9
0	1	14	29.1	32.5	1	1	2	82.2	82.7	1	5	12	19.5	-21.1	2	0	1	19.8	17.9
0	2	2	11.8	12.3	1	1	4	24.6	-23.2	1	5	14	12.1	-13.4	2	0	2	11.3	11.2
0	2	4	34.0	-42.5	1	1	5	36.2	37.0	1	6	0	19.7	19.4	2	0	3	41.6	-37.0
0	2	6	22.4	-21.9	1	1	6	9.5	-10.2	1	6	2	13.7	18.6	2	0	4	13.1	-11.5
0	2	8	10.2	10.9	1	1	7	33.0	32.1	1	6	4	12.2	-13.6	2	0	5	12.4	-14.0
0	2	10	10.4	10.9	1	1	8	16.4	-18.7	1	6	5	16.3	-12.9	2	0	6	11.8	13.1
0	3	2	20.4	23.4	1	1	9	7.7	- 9.4	1	6	6	5.5	6.9	2	0	7	44.4	38.9
0	3	4	16.8	18.5	1	1	11	16.1	-16.7	1	6	7	26.5	-23.2	2	0	8	37.7	31.6
0	3	6	9.0	-10.7	1	1	12	17.1	18.1	1	6	12	9.7	11.9	2	0	9	13.9	11.3
0	3	8	12.0	-13.0	1	1	13	6.8	- 7.7	1	6	13	15.8	-15.8	2	0	11	8.8	- 8.1
0	3	10	11.4	-12.1	1	1	14	7.5	9.0	1	6	14	6.6	- 7.4	2	0	12	4.7	5.4
0	3	12	30.4	33.1	1	1	19	4.4	- 4.6	1	7	1	45.1	41.4	2	0	14	4.7	4.4
0	3	14	28.2	29.3	1	2	0	62.4	-64.4	1	7	2	29.9	35.2	2	0	18	9.7	- 7.6
0	4	2	43.2	-44.7	1	2	1	35.0	-39.9	1	7	6	18.7	16.5	2	0	19	3.8	4.3
0	4	4	26.5	30.2	1	2	2	35.8	-41.2	1	7	7	4.6	5.3	2	2	0	10.0	11.6
0	4	6	16.1	-14.9	1	2	3	45.3	-44.6	1	7	8	11.9	9.7	2	2	1	28.6	-26.9
0	4	8	9.1	- 8.3	1	2	4	66.6	73.1	1	7	14	7.2	- 7.5	2	2	2	11.7	-10.2
0	4	12	18.4	17.5	1	2	5	28.6	27.2	1	7	15	4.5	- 5.1	2	2	3	24.7	-24.5
0	4	14	15.8	13.9	1	2	6	3.7	- 5.9	1	8	0	60.9	70.5	2	2	4	6.6	- 5.9
0	5	2	13.2	15.2	1	2	7	57.8	66.8	1	8	1	9.7	9.4	2	2	5	9.3	8.9
0	5	6	19.4	-17.6	1	2	8	5.6	- 4.6	1	8	2	28.8	31.2	2	2	7	17.1	14.5
0	5	8	31.6	-38.8	1	2	9	8.3	7.6	1	8	3	14.7	14.5	2	3	1	17.3	-15.8
0	5	10	7.8	8.0	1	2	10	5.1	- 5.7	1	8	6	12.4	-11.3	2	3	2	6.3	- 6.3
0	5	12	9.7	- 9.8	1	2	12	18.9	-18.9	1	8	9	3.7	3.9	2	3	4	23.6	13.0
0	5	14	16.9	-17.3	1	2	13	20.0	22.1	1	8	12	15.8	-15.9	2	3	5	40.4	-35.0
0	6	2	8.9	-11.3	1	2	14	14.8	15.6	1	8	14	6.5	- 5.8	2	3	6	43.9	37.9
0	6	4	37.6	44.6	1	2	16	9.1	9.6	1	9	1	9.7	9.4	2	3	7	15.7	-14.1
0	6	6	25.1	27.1	1	2	18	4.6	- 4.9	1	9	2	5.1	5.1	2	3	8	7.7	5.8
0	6	8	14.6	-14.3	1	3	1	73.3	-91.1	1	9	3	9.5	- 9.4	2	3	9	17.8	16.1
0	6	10	12.9	-12.6	1	3	2	69.3	-79.7	1	9	5	4.8	- 5.7	2	3	12	8.7	- 6.5
0	7	2	8.8	- 9.7	1	3	4	17.0	18.1	1	9	7	8.6	8.0	2	4	0	53.9	53.4
0	7	4	13.0	-11.4	1	3	5	11.1	- 9.1	1	9	9	6.3	5.8	2	4	1	34.4	-29.6
0	7	6	15.3	-16.2	1	3	6	24.2	-23.1	1	10	3	6.0	6.9	2	4	2	10.1	- 9.7
0	7	10	5.9	5.7	1	3	7	19.8	-18.4	1	10	4	6.1	- 5.7	2	4	5	12.2	11.9
0	7	12	15.9	-15.7	1	3	8	5.4	- 4.8	1	10	5	7.5	6.7	2	4	6	12.0	-12.1
0	7	14	11.6	-10.9	1	3	11	8.8	8.7	1	10	7	5.1	5.4	2	4	7	21.8	-17.1
0	8	4	5.4	- 4.8	1	3	13	9.0	7.3	1	10	13	5.7	5.2	2	4	8	22.7	-17.3
0	8	6	17.6	17.4	1	3	19	2.5	2.9	1	11	1	3.6	- 4.4	2	4	9	7.3	- 7.4
0	8	8	11.2	11.8	1	4	0	120.1	-130.3	1	11	2	11.7	-12.7	2	4	10	7.0	6.1
0	8	10	4.0	4.3	1	4	1	32.2	-30.5	1	11	14	3.7	5.1	2	4	13	5.7	- 6.6
0	9	4	8.2	8.3	1	4	2	49.9	-53.1	1	11	15	1.7	1.8	2	4	18	5.9	6.3

Table 2 (*cont.*)

h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c
2	5	1	16.8	-14.1	3	1	2	3.9	2.9	3	13	6	9.0	- 9.0	4	9	7	8.9	10.1
2	5	2	8.3	8.7	3	1	3	6.5	5.3	3	13	8	7.7	- 8.7	4	10	5	11.7	13.9
2	5	3	22.3	-20.6	3	1	4	16.2	14.5	3	14	4	6.3	9.2	4	10	7	10.8	12.5
2	5	6	32.2	-28.3	3	1	5	9.1	- 9.2	3	14	5	5.2	6.3	4	11	6	5.8	- 6.2
2	5	10	11.5	- 9.3	3	1	9	10.0	9.8	3	15	2	8.3	7.1	5	1	5	5.6	- 7.0
2	5	11	20.1	19.0	3	1	10	5.0	- 4.9	4	0	0	32.9	-31.7	5	1	6	9.0	- 9.5
2	5	13	7.3	8.1	3	2	0	10.3	-11.1	4	0	1	27.8	-30.6	5	1	7	14.9	-16.7
2	6	1	31.2	30.0	3	2	2	21.8	23.2	4	0	2	11.9	13.7	5	1	8	16.5	-18.5
2	6	2	16.5	15.8	3	2	3	13.1	12.6	4	0	3	20.6	-19.7	5	1	9	6.2	- 6.7
2	6	3	30.5	26.8	3	2	4	3.3	- 5.7	4	0	4	6.0	9.1	5	2	1	8.7	8.8
2	6	5	12.7	-11.1	3	2	5	26.3	25.3	4	0	6	20.6	-22.5	5	2	2	6.0	- 6.4
2	6	7	19.9	-17.4	3	2	6	6.4	- 5.9	4	0	8	13.1	-19.5	5	2	4	14.4	16.4
2	6	13	10.6	-10.5	3	2	7	13.1	-13.3	4	0	11	4.9	- 6.8	5	2	5	31.0	-35.3
2	6	15	8.2	- 7.7	3	2	10	7.1	- 6.8	4	0	13	6.7	- 6.1	5	2	6	16.8	19.9
2	7	1	41.8	33.7	3	2	13	19.9	-19.0	4	0	17	3.8	4.0	5	2	7	27.3	-29.9
2	7	2	21.2	20.7	3	2	14	4.0	- 6.4	4	1	1	14.3	15.6	5	2	8	5.1	- 5.7
2	7	3	14.1	10.9	3	2	15	6.5	- 7.1	4	1	3	4.9	- 5.5	5	2	9	6.7	- 6.4
2	7	5	13.3	11.5	3	3	1	43.3	40.8	4	1	6	24.7	-28.5	5	3	1	6.4	7.2
2	7	6	12.4	- 9.7	3	3	2	19.4	19.1	4	1	8	12.1	-13.0	5	3	4	3.2	3.8
2	7	12	7.9	6.6	3	3	3	10.4	- 9.9	4	1	11	4.1	6.1	5	3	6	7.8	7.0
2	8	0	9.9	-10.4	3	3	4	10.4	9.4	4	1	14	3.7	- 6.9	5	3	7	12.4	13.0
2	8	1	24.2	23.4	3	3	5	6.3	6.8	4	2	0	6.8	- 4.6	5	3	8	13.4	14.1
2	8	2	8.4	8.1	3	3	6	19.6	19.2	4	2	2	3.6	4.3	5	3	9	7.1	8.7
2	8	3	13.9	16.9	3	3	9	7.9	- 6.4	4	2	4	5.4	4.6	5	4	0	7.6	- 8.8
2	8	4	9.7	8.5	3	4	0	27.8	-24.4	4	2	5	9.5	10.7	5	4	1	7.7	7.3
2	8	10	11.4	-11.3	3	4	2	12.0	- 8.6	4	2	7	14.6	15.5	5	4	3	8.4	9.3
2	8	11	6.5	8.5	3	4	4	13.4	16.4	4	3	1	26.3	22.4	5	4	11	6.4	6.9
2	9	1	14.9	14.9	3	4	5	12.0	- 9.3	4	3	2	6.4	4.6	5	5	2	5.8	- 5.7
2	9	4	7.6	- 6.9	3	4	8	20.7	-17.6	4	3	5	10.7	- 9.0	5	5	4	5.0	- 5.6
2	9	11	14.9	-12.9	3	4	10	7.2	- 7.4	4	3	6	26.0	-26.1	5	5	6	7.6	7.5
2	9	13	7.1	- 7.4	3	5	1	32.6	23.3	4	3	7	6.6	- 7.8	5	5	7	9.5	10.2
2	10	1	8.9	- 9.9	3	5	4	13.0	-13.3	4	3	8	16.2	-14.1	5	5	8	11.7	12.2
2	10	2	10.5	-10.1	3	5	6	22.5	-21.3	4	4	0	19.7	16.9	5	6	4	8.4	- 8.9
2	10	5	9.2	8.5	3	5	8	16.6	-15.2	4	4	1	17.4	16.8	5	6	5	14.5	14.6
2	10	6	6.6	6.5	3	6	0	14.4	-12.7	4	4	2	9.9	9.0	5	6	6	8.9	- 9.6
2	10	7	9.9	9.3	3	6	2	8.7	- 9.2	4	4	3	9.9	7.7	5	6	7	9.7	9.7
2	10	13	11.5	10.5	3	6	4	23.6	22.2	4	4	6	20.2	20.7	5	7	1	9.7	-11.0
2	11	1	24.2	-23.7	3	6	5	8.7	- 7.3	4	4	7	6.0	6.5	5	7	2	6.9	- 6.1
2	11	2	16.4	-15.6	3	6	6	14.4	14.9	4	4	8	11.7	12.5	5	7	3	4.4	- 4.6
2	11	3	12.3	-11.1	3	6	7	10.9	10.8	4	5	2	5.3	- 6.1	5	7	4	5.7	- 4.9
2	11	4	10.4	-11.2	3	6	8	8.2	- 7.3	4	5	3	5.4	6.2	5	8	0	7.6	9.0
2	11	13	3.9	4.4	3	6	13	11.8	10.4	4	5	4	5.7	- 7.2	5	9	1	7.5	- 7.9
2	12	1	8.9	- 9.1	3	7	1	13.4	-12.4	4	5	5	5.8	- 6.6	6	0	0	18.1	-22.0
2	12	2	8.3	- 9.7	3	7	2	9.6	- 9.9	4	5	6	19.8	19.5	6	0	2	6.9	- 8.1
2	12	8	6.0	5.1	3	7	3	7.5	8.3	4	5	7	15.1	-14.8	6	0	3	4.9	- 4.9
2	12	9	7.1	- 6.9	3	7	4	16.1	-14.0	4	5	8	7.1	9.1	6	0	4	8.6	10.3
2	12	10	7.1	6.7	3	7	6	25.8	-22.5	4	6	2	9.4	- 7.6	6	0	5	4.2	- 4.2
2	13	1	9.1	- 7.5	3	8	0	10.8	10.6	4	6	5	22.5	-21.1	6	0	7	9.1	- 8.4
2	13	3	4.5	6.0	3	8	5	6.4	6.9	4	6	7	26.0	-24.8	6	0	8	11.4	-12.6
2	13	5	6.9	6.0	3	8	6	12.9	11.2	4	6	9	7.1	- 7.8	6	0	10	8.6	- 9.9
2	14	5	8.0	- 7.5	3	8	8	15.3	14.9	4	7	1	9.8	- 7.7	6	1	4	11.1	-14.7
2	14	7	7.3	- 6.7	3	9	6	22.6	21.4	4	7	2	11.2	-11.7	7	2	0	5.4	6.9
2	15	1	8.5	7.9	3	9	8	17.7	17.0	4	7	6	17.9	18.1	7	2	1	4.9	5.3
2	15	2	7.0	6.1	3	10	4	13.4	-13.5	4	7	7	9.1	9.3	7	2	2	5.2	6.1
2	15	3	6.7	6.5	3	10	6	10.8	-10.4	4	7	8	12.4	12.4	7	2	3	5.8	4.5
2	15	4	6.5	5.3	3	10	7	12.3	- 9.6	4	7	9	6.3	5.5	8	0	3	2.5	4.0
2	15	5	4.7	5.4	3	11	6	19.6	16.3	4	8	0	7.0	- 5.6					
2	15	6	4.4	4.0	3	12	6	10.8	- 9.0	4	8	4	5.5	- 5.5					
3	1	1	45.9	-45.4	3	12	8	6.7	- 6.0	4	8	6	11.4	-11.8					

The equations of the aromatic and the nitro group planes referred to the crystallographic axes (obtained as in Takwale & Pant, 1971), the angle between them and the deviations of atoms from these planes are given in Table 3; the direction cosines of the principal axes of the individual atomic vibration ellipsoids and the principal root-mean-square (r.m.s.) displacements are shown in Table 4 along with the angles between the principal axes of the atomic vibration ellipsoids and the aromatic plane as well as between the principal axes and the molecular axis, *i.e.* C(1)–C(4) direction.

The intramolecular bond lengths and angles along with the e.s.d.'s are shown in Fig. 1 and listed in Table 5. Corrections to N–O(1), N–O(2), C(1)–N and C(4)–C(7) bond distances arising from large thermal vibrations were evaluated as in Takwale & Pant (1971); the mean square displacements of C(1), C(7), N, O(1) and O(2) along required directions are given in Table 6. The corrections amounted to 0·030, 0·028, 0·005 and 0·026 Å for N–O(1), N–O(2), C(1)–N and C(4)–C(7) bond lengths respectively.

Table 3. *Equations of the planes*

(1) Benzene ring	$0\cdot3671x+0\cdot9219y+0\cdot1237z-1\cdot7287=0$
(2) Nitro group	$0\cdot4003x+0\cdot9128y+0\cdot0811z-1\cdot8919=0$

Table 3 (*cont.*)

Angle between the benzene plane and the plane of the nitro group = 3·0°

Deviations of atoms from different planes (Å)

	Planes (1)	(2)
C(1)	−0·005	−0·142
C(2)	0·004	
C(3)	−0·001	
C(4)	0·000	
C(5)	−0·001	
C(6)	0·004	
C(7)	0·002	
N	0·057	
O(1)	0·017	
O(2)	0·033	

Table 4. *Magnitudes and direction cosines of the principal axes of the atomic vibration ellipsoids, the angles between the principal axes and the aromatic plane and those between the principal axes and the molecular axis (i.e. the* C(1)–C(4) *direction)*

	Axis	$\sqrt{\bar{u}^2}$	cos α_1	cos α_2	cos α_3	Angle with benzene plane	Angle with the molecular axis
C(1)	1	0·226 Å	0·878	0·232	−0·418	29°	38°
	2	0·206	0·119	0·740	0·662	54	55
	3	0·194	−0·463	0·632	−0·622	20	70
C(2)	1	0·259	−0·375	0·328	0·867	15	16
	2	0·209	0·143	0·945	−0·296	62	77
	3	0·184	0·916	−0·013	0·401	22	82
C(3)	1	0·263	−0·153	0·332	0·931	21	26
	2	0·234	0·006	0·942	−0·335	56	79
	3	0·202	0·988	0·046	0·146	25	67
C(4)	1	0·256	0·687	−0·495	0·533	8	88
	2	0·228	−0·404	0·350	0·845	16	16
	3	0·213	0·605	0·795	−0·040	72	74
C(5)	1	0·279	0·623	−0·448	−0·641	15	24
	2	0·249	−0·612	−0·790	−0·043	73	78
	3	0·195	0·487	−0·419	0·766	6	70
C(6)	1	0·262	−0·070	0·630	0·774	41	41
	2	0·218	0·735	0·557	−0·387	47	48
	3	0·212	0·674	−0·542	0·502	11	89
C(7)	1	0·351	0·830	−0·091	0·550	17	89
	2	0·313	−0·207	−0·966	0·152	72	82
	3	0·206	−0·518	0·240	0·821	8	8
N	1	0·256	0·532	−0·166	0·830	8	66
	2	0·248	−0·229	0·915	0·331	53	61
	3	0·210	0·815	0·366	−0·449	36	39
O(1)	1	0·372	0·315	0·875	0·368	75	77
	2	0·303	−0·275	0·456	−0·847	12	57
	3	0·221	0·908	−0·165	−0·384	8	35
O(2)	1	0·430	0·314	0·933	0·178	86	86
	2	0·281	0·933	−0·267	−0·243	4	44
	3	0·211	0·179	−0·242	0·954	2	47

Table 5. *Intramolecular bond lengths and angles*

	Bond lengths Uncorrected	Corrected	e.s.d.	Bond angles	
C(1)–C(2)	1·408 Å		0·007 Å	C(1)–C(2)–C(3)	116·7 ± 0·4°
C(2)–C(3)	1·382		0·007	C(2)–C(3)–C(4)	122·8 ± 0·5
C(3)–C(4)	1·388		0·007	C(3)–C(4)–C(5)	117·5 ± 0·5
C(4)–C(5)	1·404		0·008	C(4)–C(5)–C(6)	121·3 ± 0·5
C(5)–C(6)	1·383		0·008	C(5)–C(6)–C(1)	119·1 ± 0·5
C(6)–C(1)	1·351		0·007	C(6)–C(1)–C(2)	122·7 ± 0·5
C(4)–C(7)	1·502	1·528 Å	0·009	C(6)–C(1)–N	119·6 ± 0·4
C(1)–N	1·477	1·482	0·007	C(2)–C(1)–N	117·6 ± 0·4
N——O(1)	1·216	1·246	0·007	C(1)–N——O(1)	118·4 ± 0·5
N——O(2)	1·211	1·239	0·007	C(1)–N——O(2)	118·5 ± 0·5
C(2)–H(1)	1·01		0·057	O(1)–N——O(2)	122·8 ± 0·4

Table 5 (*cont.*)

	Bond lengths Uncorrected	Bond lengths Corrected	e.s.d.
C(3)–H(2)	0·95		0·059
C(5)–H(3)	0·90		0·062
C(6)–H(4)	0·96		0·060
C(7)–H(5)	0·89		0·070
C(7)–H(6)	0·69		0·072
C(7)–H(7)	0·66		0·069

Bond angles	
C(3)–C(4)–C(7)	121·6 ± 0·5
C(5)–C(4)–C(7)	120·9 ± 0·5

Table 6. *Some mean square displacements* (Å^2 × 10^3)

	Direction of displacement* Normal to the molecular plane†		Direction of displacement* In the plane normal to the bond	Direction of displacement* Parallel to the bond
O(1)	133		90	58
O(2)	183		78	61
C(1)	48		40	48
N	55	(*a*)	60 O(1)	49 O(1)
		(*b*)	40 O(2)	65 O(2)
		(*c*)	49 C(1)	51 C(1)
C(4)	45		65	53
C(7)	99		121	44

* Values parallel and normal to the bond for C(1) and C(4) are given only for C(1)–N and C(4)–C(7) bonds respectively. The atoms listed besides certain values in this Table indicate the direction of the bond in question.

† The vibration directions of O(1), O(2) and N are with respect to the plane of the nitro group whereas the vibration directions of C(4) and C(7) are with respect to the benzene plane.

Discussion

The C(1)–C(6) bond length in *p*-nitrotoluene, 1·351 ± 0·008 Å appears to be significantly shorter than the other aromatic bonds. The average length of the other five aromatic bonds, 1·393 Å is normal. The average length of the central bonds C(2)–C(3) and C(5)–C(6) is 1·383 Å while that of the other three bonds C(1)–C(2), C(3)–C(4) and C(4)–C(5) is 1·400 Å; these results agree within experimental error with those in *p*-toluic acid and the other compounds mentioned in Takwale & Pant (1971).

The C–N bond length of 1·482 ± 0·007 Å (1·477 Å without correction for librational effects) agrees with those found in *p*-nitrobenzoic acid, 1·480 ± 0·007 Å (uncorrected) (Sakore & Pant, 1966) and *m*-dinitrobenzene, 1·491 ± 0·008 and 1·494 ± 0·009 Å (Trotter & Williston, 1966) but is a little shorter in *p*-nitroaniline, 1·460 ± 0·007 Å (Trueblood, Goldish & Donohue, 1961), *α*-*p*-nitrophenol, 1·442 ± 0·006 Å (uncorrected at 90°K, Coppens & Schmidt, 1965*a*) and *β*-*p*-nitrophenol, 1·450 ± 0·003 Å (Coppens & Schmidt, 1965*b*). These results probably indicate that unlike the cases of *p*-nitroaniline and *p*-nitrophenol, there is no appreciable resonance interaction between the *para* substituents in *p*-nitrotoluene. Dipole moment studies appear to support this view. The sum of the dipole moments of toluene and nitrobenzene, 0·35 and 3·95D respectively, is nearly equal to the dipole moment of *p*-nitrotoluene, 4·35D. On the other hand in *p*-nitroaniline, the dipole moment (6·10D) exceeds the sum of the dipole moments of aniline and nitrobenzene, 1·53 and 3·95D respectively, by about 0·62D, indicating

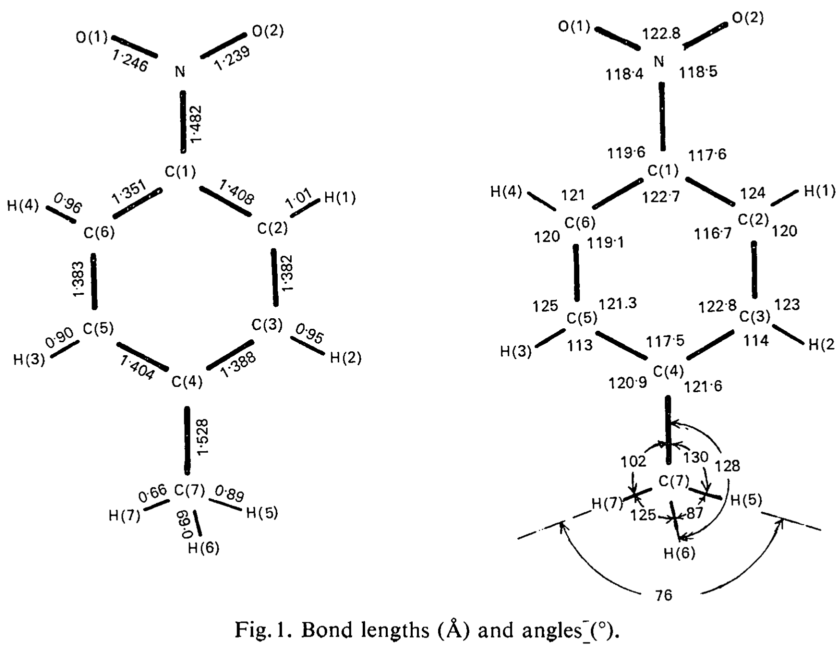

Fig. 1. Bond lengths (Å) and angles (°).

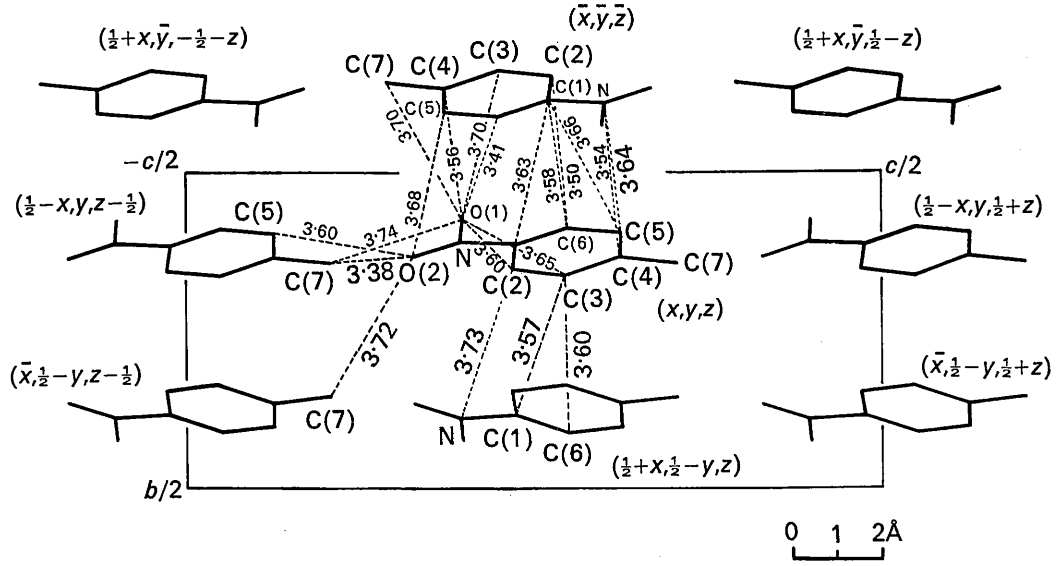

Fig. 2. The structure of *p*-nitrotoluene projected on (100).

extra resonance interaction between the substituents (Ferguson, 1963).

The nitrogen atom N is 0·056 Å away from the aromatic plane; the corresponding deviations in other similar molecules are 0·049 Å in *p*-nitrobenzoic acid, 0·037 and 0·038 Å in α- and β-*p*-nitrophenol respectively and 0·019 Å in *p*-nitroaniline. The carbon atom C(1) is 0·142 Å away from the nitro group plane. The corresponding deviations in other molecules are 0·121 Å in *p*-nitrobenzoic acid and approximately 0·01 Å in *p*-nitroaniline and α- and β-*p*-nitrophenol. The differences in atomic deviations mentioned above in different structures may partly be due to the differences in the intermolecular interactions in them. However, strong resonance interaction between the nitro group and the rest of the molecule in *p*-nitroaniline and *p*-nitrophenol seems to be responsible for the lesser deviation of the nitrogen atom from the aromatic plane and of the carbon atom (to which the nitro group is attached) from the nitro group plane in these molecules than in *p*-nitrotoluene and *p*-nitrobenzoic acid.

The carbon atom C(7) of the methyl group lies on the aromatic plane. The C(4)–C(7) bond length, 1·528 ± 0·009 Å (uncorrected value, 1·502 Å) is not significantly different from the corresponding length in *p*-toluic acid, 1·514 ± 0·011 Å (uncorrected value, 1·499 Å, Takwale & Pant, 1971).

The torsional oscillation of the nitro group implied by the r.m.s. displacements of the oxygen atoms is more severe in *p*-nitrotoluene than in *p*-nitroaniline and β-*p*-nitrophenol. This is expected in view of the presence of hydrogen bonds in the latter structures. Table 4 shows that the thermal anisotropy is more pronounced in atom O(2) than in O(1) and this appears to be due to the difference in the intermolecular interactions for the two atoms. The arrangement of molecules in the unit cell is shown in Fig. 2 in which the intermolecular distances (< 3·8 Å) are also shown. It is seen that atom O(2) has fewer intermolecular contacts than O(1). As in the structure of *p*-toluic acid, the methyl group has a considerable vibration normal to the C(4)–C(7) bond. A comparison of Table 4 with Table 4 of Takwale & Pant (1971) shows that the magnitudes of the principal axes of the atomic vibration ellipsoids of the carbon atoms of the methyl group in the two structures are similar, the corresponding values being 0·351, 0·313, 0·206 Å in *p*-nitrotoluene and 0·355, 0·278 and 0·203 Å in *p*-toluic acid; the orientations of the vibration ellipsoids with respect to the benzene plane and the molecular axis are also the same within 12°.

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