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The Crystal Structure of 2,4,6-Trinitro-*m*-xylene (TNX)

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The crystal structure of 2,4,6-trinitro-*m*-xylene has been determined with visually estimated X-ray intensity data, and the atomic parameters were refined by full-matrix least-squares methods to a value of 0·071 for the discrepancy index, *R*. The dimensions of the orthorhombic unit cell are $a_o = 5{\cdot}742 \pm 0{\cdot}011$, $b_o = 14{\cdot}996 \pm 0{\cdot}006$, and $c_o = 11{\cdot}384 \pm 0{\cdot}006$ Å. The four molecules in the unit cell lie on twofold axes in the space group *Pbcn*. The benzene ring is planar to within the precision of the analysis. The planes of the nitro groups in the 4 and 6 positions are rotated by angles of 35·7°, and the one in the 2 position is rotated by an angle of 75·2° with respect to the plane of the benzene ring. Bond lengths in the molecule are within expected ranges; however, the bond angles of the benzene ring deviate significantly from 120°.

Introduction

The analysis of the crystal structure of 2,4,6-trinitro-*m*-xylene (TNX) is part of a program to study the molecular packing and the effect of crowded substituents on molecular structure in a number of polynitro aromatic compounds. It is of particular interest to compare the structure of TNX with that of 2,4,6-trinitrotoluene (TNT) not only because of their chemical similarity, but because of their great differences in certain physical properties, such as melting point (180·2° for TNX *vs.* 80·9° for TNT). Because of certain crystallographic similarities, the TNX structure was the key to the elucidation of the structures of the monoclinic and orthorhombic polymorphs of TNT. These structures are now being refined and will be reported later.

Experimental

Excellent crystals of TNX can be grown by slow evaporation of ethanol or acetone solutions at room temperature. TNX forms small, colorless or pale yellow prisms, elongated in one direction and of nearly uniform cross section, which belong to the orthorhombic bipyramidal class. A typical crystal grown from acetone showed the forms {010}, {001}, {021}, and {111}.

The dimensions of the unit cell, measured from rotation and zero-layer Weissenberg photographs taken about the *a* axis at room temperature, are (λ of Cu $K\alpha = 1{\cdot}5418$ Å) $a_o = 5{\cdot}742 \pm 0{\cdot}011$, $b_o = 14{\cdot}996 \pm 0{\cdot}006$, and $c_o = 11{\cdot}384 \pm 0{\cdot}006$ Å. The experimental density of TNX, obtained by flotation in a mixture of carbon tetrachloride and ethylene dibromide, is 1·615 g.ml^{-1}; the density calculated for four molecules of $C_8H_7N_3O_6$ per unit cell is 1·634 g.ml^{-1}.

The space group extinctions observed were: $0kl$ present only with $k=2n$; $h0l$ present only with $l=2n$; and $hk0$ present only with $h+k=2n$. The hkl reflections were present in all orders. These extinctions uniquely determine the space group as *Pbcn*.

Intensity data for the structure analysis were measured visually from sets of multiple-film equi-inclination Weissenberg photographs, taken with nickel-filtered Cu $K\alpha$ radiation. The layer lines $0kl$ through $4kl$ about the *a* axis were used for this purpose. Of the 1110 unique reflections possible from a crystal of TNX with Cu $K\alpha$ radiation, 902 (81 %) were within the range of the camera on these layer lines. 732 reflections of measurable intensity were found. Lorentz and polarization corrections were applied in the usual way; in addition, the upper layer line reflections were corrected for spot extension by the method of Phillips (1954). No corrections were made for absorption or extinction.

Determination and refinement of the structure

Since the general positions in the space group *Pbcn* are eightfold and there are only four molecules of TNX in the unit cell, the molecules must exhibit some symmetry of the space group. From the shape and possible symmetry of a TNX molecule, this can only be the twofold axes parallel to the *b* axis. A trial model of the molecule was obtained from the sharpened Patterson projection on (100). This model was positioned along the twofold axes by packing considerations and inferences from the Patterson projection to obtain a satisfactory trial structure. Final refinement of the projected structure was carried out by Fourier and least-squares methods.

The initial *x* parameters for the three-dimensional refinement were obtained from assumed molecular geometry, and were improved by $1kl$ generalized projections. At this point, all of the available data were used in a series of full-matrix least-squares refinements. The weighting scheme employed was that proposed by Hughes (1941). Unobserved reflections were given zero weights in all of the calculations. The scattering fac-

Table 1. *Observed and calculated structure amplitudes*

Unobserved reflections are indicated by a minus sign.
Asterisks mark observed reflections given zero weight in the final least-squares refinements.

H	K	L	F_o	F_c
0	0	0	----	496.0
*0	0	2	66.4	75.3
0	0	4	50.6	50.8
0	0	6	66.0	63.9
0	0	8	12.5	12.4
0	0	10	16.3	17.2
0	0	12	20.2	19.1
0	0	14	16.9	16.4
*0	2	0	46.7	74.7
0	2	1	11.9	11.8
0	2	2	40.2	40.6
0	2	3	39.8	36.9
0	2	4	69.6	75.5
0	2	5	28.6	25.6
0	2	6	8.8	9.1
0	2	7	12.6	12.2
0	2	8	3.9	4.0
0	2	9	5.7	5.6
0	2	10	8.6	8.8
0	2	11	5.0	4.7
0	2	12	4.3	4.0
0	2	13	11.1	10.4
0	2	14	9.2	8.7
*0	4	0	43.1	48.5
0	4	1	24.4	25.1
0	4	2	56.9	61.9
0	4	3	69.5	75.7
0	4	4	3.7	2.1
0	4	5	31.2	28.2
0	4	6	2.4	3.2
0	4	7	54.1	51.0
0	4	8	14.9	14.2
0	4	9	8.4	7.2
0	4	10	11.5	10.6
0	4	11	-2.6	0.2
0	4	12	5.8	5.7
0	4	13	4.8	4.2
0	4	14	6.5	6.5
0	6	0	34.0	33.0
*0	6	1	61.8	77.0
0	6	2	18.8	18.9
0	6	3	21.8	21.2
0	6	4	35.6	34.8
0	6	5	12.2	13.2
0	6	6	19.1	18.0
0	6	7	17.4	18.0
0	6	8	7.8	8.1
0	6	9	2.8	2.4
0	6	10	14.2	12.7
0	6	11	12.0	11.1
0	6	12	3.8	3.9
0	6	13	7.2	7.2
0	6	14	-0.7	4.0
*0	8	0	62.1	72.3
0	8	1	16.0	15.8
0	8	2	9.3	8.7
0	8	3	10.5	10.4
0	8	4	2.7	3.0
0	8	5	18.4	17.3
0	8	6	9.9	9.8
0	8	7	17.2	16.2
0	8	8	13.6	13.6
0	8	9	13.1	13.0
0	8	10	-2.6	1.7
0	8	11	2.9	3.7
0	8	12	13.6	12.6
0	8	13	4.0	3.7
0	10	0	17.9	16.8
0	10	1	27.9	31.3
0	10	2	4.8	5.4
0	10	3	27.9	29.5
0	10	4	8.3	9.1
0	10	5	11.8	12.0
0	10	6	22.8	24.2
0	10	7	19.5	21.0
0	10	8	32.7	32.8
0	10	9	10.4	9.9
0	10	10	4.0	3.6
0	10	11	5.0	5.3
0	10	12	-1.6	0.5
0	12	0	10.5	9.7
0	12	1	-2.6	0.0
0	12	2	-2.6	2.5
0	12	3	21.1	21.6
0	12	4	-2.8	0.6
0	12	5	28.7	29.9
0	12	6	-2.8	1.8
0	12	7	33.1	30.6
0	12	8	-2.5	1.8
0	12	9	6.8	6.6
0	12	10	2.2	2.5
0	12	11	4.3	4.4
0	14	0	11.0	11.4
0	14	1	10.6	12.9
0	14	2	5.4	6.8
0	14	3	4.6	4.8
0	14	4	5.0	6.4
0	14	5	-2.6	0.3
0	14	6	6.7	6.4
0	14	7	2.3	3.1
0	14	8	3.2	2.8
0	14	9	4.1	4.3
0	14	10	4.2	4.7
0	16	0	16.0	16.4
0	16	1	5.0	4.9
0	16	2	5.9	7.1
0	16	3	4.1	4.1
0	16	4	-2.3	0.4
0	16	5	4.0	4.1
0	16	6	1.9	2.0
0	16	7	-1.7	1.0
0	16	8	-1.1	0.7
0	18	0	13.2	11.7
0	18	1	5.2	4.0
0	18	2	4.9	5.4
0	18	3	7.6	6.3
0	18	4	9.7	9.9
0	18	5	-1.1	1.1
1	3	0	7.3	7.7
1	5	0	38.7	47.4
1	7	0	7.3	7.2
1	9	0	23.7	24.9
1	11	0	17.6	18.8
1	13	0	9.8	9.3
1	15	0	8.8	10.1
1	17	0	5.7	5.0
1	19	0	2.0	1.5
1	1	1	14.3	14.3
1	2	1	7.2	6.7
1	3	1	5.0	4.8
1	4	1	44.0	56.4
1	5	1	37.4	38.7
1	6	1	10.1	9.7
1	7	1	16.4	14.8
1	8	1	6.0	5.9
1	9	1	3.3	3.9
1	10	1	11.9	11.8
1	11	1	-2.1	0.9
1	12	1	12.3	10.8
1	13	1	3.2	2.5
1	14	1	15.5	17.1
1	15	1	5.0	5.0
1	16	1	9.5	9.9
1	17	1	-1.8	1.4
1	18	1	-1.4	1.1
1	19	1	2.4	3.0
*1	0	2	62.0	134.0
*1	1	2	48.2	63.1
*1	2	2	50.8	67.1
1	3	2	29.6	32.0
1	4	2	43.8	50.2
1	5	2	11.2	9.8
1	6	2	12.9	13.2
1	7	2	26.0	27.6
1	8	2	19.4	17.1
1	9	2	5.2	4.5
1	10	2	-2.0	0.8
1	11	2	8.3	8.5
1	12	2	5.8	4.7
1	13	2	2.8	2.4
1	14	2	19.1	20.7
1	15	2	4.0	4.0
1	16	2	3.3	3.4
1	17	2	2.0	1.2
1	18	2	7.4	6.7
1	19	2	-0.7	0.8
*1	1	3	73.7	93.2
1	2	3	39.2	38.5
1	3	3	40.9	43.2
1	4	3	10.8	11.2
1	5	3	30.2	31.5
1	6	3	-1.6	1.9
1	7	3	42.0	40.8
1	8	3	29.0	27.3
1	9	3	-2.0	0.2
1	10	3	16.1	17.2
1	11	3	-2.2	0.8
1	12	3	9.3	10.4
1	13	3	5.6	5.3
1	14	3	12.0	13.0
1	15	3	6.9	6.5
1	16	3	-1.9	0.6
1	17	3	3.5	3.4
1	18	3	1.4	1.5
1	0	4	52.0	56.2
1	1	4	30.2	27.5
1	2	4	45.4	46.7
1	3	4	41.4	40.1
1	4	4	19.5	18.9
1	5	4	30.3	27.6
1	6	4	14.7	13.2
1	7	4	27.9	26.2
1	8	4	3.6	3.5
1	9	4	5.9	6.3
1	10	4	8.6	8.8
1	11	4	23.4	24.1
1	12	4	14.0	14.9
1	13	4	7.9	7.5
1	14	4	-2.2	0.4
1	15	4	-2.0	0.3
1	16	4	8.0	7.5
1	17	4	2.6	1.7
1	18	4	5.0	5.9
1	1	5	4.8	4.1
1	2	5	40.4	37.0
1	3	5	5.6	5.0
1	4	5	29.1	26.0
1	5	5	6.3	4.9
1	6	5	19.4	18.1
1	7	5	-2.0	0.5
1	8	5	20.3	19.9
1	9	5	11.2	11.7
1	10	5	31.6	33.1
1	11	5	14.2	15.5
1	12	5	12.2	11.7
1	13	5	-2.3	1.0
1	14	5	5.3	5.8
1	15	5	4.0	3.9
1	16	5	6.6	6.2
1	17	5	5.4	4.9
1	18	5	-0.7	0.4
1	0	6	18.3	16.1
1	1	6	4.3	4.2
1	2	6	17.6	14.5
1	3	6	14.7	12.2
1	4	6	21.0	19.4
1	5	6	4.6	4.8
1	6	6	-2.0	0.5
1	7	6	-2.1	0.4
1	8	6	15.1	15.0
1	9	6	10.7	10.6
1	10	6	15.0	16.1
1	11	6	9.4	9.7
1	12	6	10.7	11.0
1	13	6	-2.2	1.5
1	14	6	3.4	3.3
1	15	6	-1.8	0.1
1	16	6	6.5	6.4
1	17	6	6.7	6.7
1	1	7	27.0	26.8
1	2	7	9.0	8.0
1	3	7	25.8	25.3
1	4	7	19.1	17.5
1	5	7	10.1	10.0
1	6	7	24.4	23.1
1	7	7	14.6	14.3
1	8	7	7.6	7.0
1	9	7	8.4	8.5
1	10	7	3.3	4.0
1	11	7	15.1	15.3
1	12	7	12.4	11.9
1	13	7	-2.0	1.8
1	14	7	5.3	4.8
1	15	7	-1.6	0.6
1	16	7	4.8	4.7
1	0	8	7.3	7.4
1	1	8	-2.1	0.8
1	2	8	3.5	3.2
1	3	8	6.7	6.1
1	4	8	10.2	11.4
1	5	8	2.6	1.9
1	6	8	7.6	7.3
1	7	8	-2.3	1.6
1	8	8	3.5	3.1
1	9	8	7.1	7.2
1	10	8	13.7	14.9
1	11	8	12.4	12.4
1	12	8	2.0	2.0
1	13	8	2.2	2.2
1	14	8	4.4	4.3
1	15	8	2.9	2.6
1	16	8	-0.7	0.8
1	1	9	11.7	10.5
1	2	9	-2.2	2.4
1	3	9	-2.3	1.0
1	4	9	15.2	14.5
1	5	9	10.8	10.8
1	6	9	9.8	9.5
1	7	9	2.3	2.5
1	8	9	7.2	6.8
1	9	9	-2.2	0.8
1	10	9	6.8	6.8
1	11	9	8.3	7.3
1	12	9	4.7	4.4
1	13	9	4.3	4.1
1	14	9	-1.3	0.5
1	15	9	-0.9	2.0
1	0	10	18.7	19.6
1	1	10	3.5	3.7
1	2	10	3.2	3.5
1	3	10	5.2	5.5
1	4	10	11.6	10.9
1	5	10	12.0	11.6
1	6	10	-2.3	1.0
1	7	10	10.2	10.2
1	8	10	11.9	12.9
1	9	10	-2.0	0.4
1	10	10	13.1	13.1
1	11	10	13.0	12.2
1	12	10	3.2	3.0
1	13	10	-1.2	0.8
1	14	10	-0.5	2.5
1	1	11	12.9	13.2
1	2	11	7.9	7.8
1	3	11	-2.3	1.2
1	4	11	-2.2	0.9
1	5	11	5.4	5.4
1	6	11	-2.1	0.5
1	7	11	-2.0	2.1
1	8	11	-1.9	1.2
1	9	11	-1.8	0.9
1	10	11	-1.6	0.8
1	11	11	5.5	5.3
1	12	11	3.0	2.8
1	0	12	9.2	8.5
1	1	12	3.5	3.5
1	2	12	8.6	7.5
1	3	12	-2.0	0.1
1	4	12	3.5	3.0
1	5	12	1.9	2.0
1	6	12	6.2	5.9
1	7	12	6.4	5.8
1	8	12	-1.6	0.4
1	9	12	3.0	2.7
1	10	12	3.0	3.3
1	11	12	-0.5	1.9
1	1	13	4.0	3.7
1	2	13	1.7	1.5
1	3	13	2.4	2.3
1	4	13	1.9	2.1
1	5	13	1.5	1.8
1	6	13	4.0	4.4
1	7	13	-1.2	0.1
1	8	13	4.8	5.8
1	0	14	4.3	3.8
1	1	14	4.5	4.1
1	2	14	3.4	3.0
1	3	14	2.0	2.0
1	4	14	2.4	2.9
1	5	14	-0.9	1.5
2	2	0	20.1	20.5
*2	4	0	51.0	67.9
2	6	0	29.0	28.6
2	8	0	9.7	9.2
2	10	0	9.8	9.8
2	12	0	18.0	18.4
2	14	0	9.4	9.9
2	16	0	6.5	6.8
2	18	0	14.9	16.0
2	1	1	1.0	0.8
2	2	1	13.6	13.0
2	3	1	7.4	6.5
2	4	1	17.2	15.9
2	5	1	4.9	5.6
2	6	1	8.8	8.3
2	7	1	3.3	2.4
2	8	1	18.3	19.7
2	9	1	26.4	27.5
2	10	1	5.2	5.0
2	11	1	8.7	9.3
2	12	1	17.6	18.0
2	13	1	2.8	3.5
2	14	1	8.1	7.9
2	15	1	5.4	5.3
2	16	1	5.6	6.1
2	17	1	4.1	3.4
2	18	1	-1.2	1.6
2	0	2	41.9	44.8
2	1	2	15.8	14.3
2	2	2	12.6	12.1
2	3	2	38.0	44.3
2	4	2	27.5	27.9
2	5	2	22.2	22.2
2	6	2	9.9	10.1
2	7	2	3.5	3.3
2	8	2	8.4	8.1
2	9	2	7.7	7.6
2	10	2	17.9	19.4
2	11	2	14.8	14.6
2	12	2	2.3	2.4
2	13	2	11.2	10.3
2	14	2	11.8	11.6
2	15	2	7.4	7.3
2	16	2	1.9	1.8
2	17	2	-1.6	0.1
2	18	2	5.4	5.4
2	1	3	37.7	35.1
2	2	3	14.0	13.6
2	3	3	2.8	3.5
2	4	3	43.8	42.3
2	5	3	10.8	11.7
2	6	3	10.5	10.1
2	7	3	-1.9	1.5
2	8	3	13.8	13.7
2	9	3	33.2	35.5
2	10	3	6.4	7.0
2	11	3	7.4	7.8
2	12	3	15.9	16.9
2	13	3	4.1	4.5
2	14	3	18.2	18.1
2	15	3	-2.1	0.4
2	16	3	14.4	13.3
2	17	3	2.6	2.1
2	18	3	2.8	2.8
2	0	4	40.7	40.9
2	1	4	6.1	6.3
2	2	4	11.9	10.5
2	3	4	35.0	33.3
2	4	4	15.4	15.8
2	5	4	19.9	15.3
2	6	4	11.2	11.1
2	7	4	3.9	3.5
2	8	4	-2.1	0.7
2	9	4	7.0	6.9
2	10	4	24.1	26.7
2	11	4	2.8	3.0
2	12	4	6.3	6.8
2	13	4	15.7	16.8
2	14	4	12.0	11.1
2	15	4	-2.0	0.0
2	16	4	4.5	4.6
2	17	4	3.8	4.1
2	1	5	41.3	38.7
2	2	5	19.8	19.0
2	3	5	5.8	4.6
2	4	5	2.4	1.6
2	5	5	19.4	18.0
2	6	5	25.4	25.0
2	7	5	6.5	6.4
2	8	5	14.8	14.9
2	9	5	8.9	8.6
2	10	5	5.3	5.6
2	11	5	5.3	5.9
2	12	5	2.9	3.1
2	13	5	-2.2	0.4
2	14	5	-2.1	1.4
2	15	5	8.6	8.0
2	16	5	-1.6	0.8
2	17	5	2.5	2.7
2	0	6	19.0	17.5
2	1	6	11.7	11.1
2	2	6	12.4	12.2
2	3	6	10.6	10.7
2	4	6	34.7	38.8
2	5	6	16.6	15.8
2	6	6	7.0	6.8
2	7	6	5.2	5.1
2	8	6	12.7	13.2
2	9	6	-2.3	0.1
2	10	6	-2.3	0.1
2	11	6	2.9	2.7
2	12	6	7.9	8.6
2	13	6	9.9	10.2
2	14	6	4.2	3.8
2	15	6	-1.7	0.9
2	16	6	-1.2	0.3
2	1	7	-2.1	1.2
2	2	7	5.9	5.7
2	3	7	-2.1	1.4
2	4	7	4.0	3.4
2	5	7	9.6	8.8
2	6	7	7.1	6.8
2	7	7	7.9	7.9
2	8	7	-2.3	2.5
2	9	7	5.5	5.8
2	10	7	-2.3	1.4
2	11	7	4.2	4.2
2	12	7	3.6	3.5
2	13	7	-1.9	0.5
2	14	7	6.4	6.7
2	15	7	3.1	2.5
2	16	7	1.6	2.0
2	0	8	32.0	33.1
2	1	8	14.5	12.9
2	2	8	4.4	4.4
2	3	8	-2.3	1.4
2	4	8	3.8	3.4
2	5	8	6.1	6.3
2	6	8	3.6	3.8
2	7	8	4.2	4.2
2	8	8	15.8	16.5
2	9	8	-2.3	1.7
2	10	8	3.9	3.2
2	11	8	3.8	3.1
2	12	8	1.9	2.3
2	13	8	3.5	3.4
2	14	8	4.2	3.8
2	15	8	4.5	4.7
2	1	9	16.8	16.9
2	2	9	-2.3	0.8
2	3	9	4.6	5.2
2	4	9	6.3	6.5
2	5	9	-2.3	1.1
2	6	9	-2.3	0.3
2	7	9	4.2	4.6
2	8	9	9.3	9.4
2	9	9	-2.1	0.8
2	10	9	5.8	5.4
2	11	9	-1.9	0.0
2	12	9	4.6	4.6
2	13	9	3.2	2.9
2	14	9	6.8	6.7
2	0	10	13.2	12.8
2	1	10	3.9	3.6
2	2	10	9.3	8.1
2	3	10	4.2	4.8
2	4	10	-2.3	0.7
2	5	10	-2.3	0.2
2	6	10	-2.2	0.5
2	7	10	5.1	5.1
2	8	10	-2.1	0.9
2	9	10	-1.9	0.6
2	10	10	13.6	14.1
2	11	10	7.7	7.4
2	12	10	2.9	2.8
2	13	10	5.3	6.1
2	1	11	8.1	7.8
2	2	11	3.1	2.8
2	3	11	5.4	4.9
2	4	11	4.6	4.4
2	5	11	-2.1	0.3
2	6	11	11.9	10.7
2	7	11	1.9	1.8
2	8	11	3.6	3.3
2	9	11	10.8	11.1
2	10	11	-1.4	0.5
2	11	11	4.5	4.4
2	0	12	3.3	3.0
2	1	12	-2.0	0.0
2	2	12	-1.9	0.8
2	3	12	6.4	6.0
2	4	12	9.0	9.2
2	5	12	6.3	5.4
2	6	12	-1.7	0.5
2	7	12	1.6	1.7
2	8	12	-1.4	0.7
2	9	12	2.7	2.9
2	10	12	-0.5	5.4
2	1	13	-1.6	0.2
2	2	13	3.7	3.7
2	3	13	-1.4	0.9
2	4	13	2.4	2.6
2	5	13	2.2	1.9
2	6	13	1.1	1.4
2	7	13	-0.9	1.2
2	0	14	2.8	3.2
2	1	14	-0.9	0.2
2	2	14	2.0	2.4
2	3	14	-0.5	0.8
3	3	0	20.2	18.4
3	5	0	35.5	38.6
3	7	0	3.6	5.0
3	9	0	10.3	9.3
3	11	0	28.3	31.2
3	13	0	2.1	2.8
3	15	0	2.6	2.0
3	17	0	12.7	12.4
3	1	1	8.2	6.5
3	2	1	19.8	21.2
3	3	1	31.6	30.2
3	4	1	16.7	16.2
3	5	1	12.1	12.3
3	6	1	8.6	8.9
3	7	1	24.6	24.5
3	8	1	8.6	9.0
3	9	1	18.4	19.4
3	10	1	10.9	11.6
3	11	1	28.2	31.6
3	12	1	8.5	10.4
3	13	1	-2.1	1.5
3	14	1	5.2	4.7
3	15	1	7.8	7.7
3	16	1	3.9	3.9
3	17	1	9.4	8.8
3	0	2	32.4	35.2
3	1	2	15.0	13.6
3	2	2	6.5	5.5
3	3	2	10.6	9.6
3	4	2	11.4	11.4
3	5	2	9.8	7.7
3	6	2	-1.8	1.5
3	7	2	9.0	9.5
3	8	2	5.6	6.2
3	9	2	2.0	2.0
3	10	2	-2.1	1.5
3	11	2	19.1	21.1
3	12	2	4.2	4.6
3	13	2	3.0	3.1
3	14	2	3.9	3.2
3	15	2	8.7	8.2
3	16	2	-1.4	0.4
3	17	2	5.6	5.0
3	1	3	10.2	9.6
3	2	3	3.0	2.2
3	3	3	7.8	8.0
3	4	3	-1.7	0.8
3	5	3	20.5	20.6
3	6	3	7.3	7.6
3	7	3	3.3	2.7
3	8	3	3.4	2.8
3	9	3	19.9	20.9
3	10	3	2.5	2.6
3	11	3	-2.2	1.2
3	12	3	-2.1	1.9
3	13	3	7.1	6.6
3	14	3	-1.9	0.4
3	15	3	6.1	5.8
3	16	3	2.2	2.3
3	17	3	-0.9	1.2
3	0	4	32.2	31.9
3	1	4	6.6	6.3
3	2	4	10.7	10.3
3	3	4	4.4	3.0
3	4	4	14.9	15.2
3	5	4	7.4	7.9
3	6	4	-2.0	0.1
3	7	4	8.8	9.3
3	8	4	12.9	13.7
3	9	4	6.4	6.2
3	10	4	6.0	6.6
3	11	4	5.8	6.2
3	12	4	-2.1	0.7
3	13	4	-2.0	1.0
3	14	4	5.3	5.3
3	15	4	8.0	8.0
3	16	4	-1.2	0.4
3	17	4	-0.5	0.1
3	1	5	21.4	20.3
3	2	5	5.4	4.6
3	3	5	5.5	4.3
3	4	5	10.9	10.5
3	5	5	2.4	1.4
3	6	5	3.7	3.5
3	7	5	8.6	8.0
3	8	5	-2.1	2.2
3	9	5	6.6	7.0
3	10	5	5.6	6.2
3	11	5	-2.1	1.5
3	12	5	2.0	2.5
3	13	5	-1.9	0.8
3	14	5	4.9	4.4
3	15	5	4.7	4.2
3	16	5	3.7	4.1
3	0	6	3.2	2.6
3	1	6	23.6	23.9
3	2	6	10.1	9.5
3	3	6	-2.0	0.4
3	4	6	8.5	7.3
3	5	6	8.4	7.6
3	6	6	6.6	6.4
3	7	6	10.4	10.6
3	8	6	-2.1	0.8
3	9	6	8.4	9.3
3	10	6	3.4	3.8
3	11	6	-2.0	0.2
3	12	6	-2.0	1.2
3	13	6	11.5	10.7
3	14	6	-1.5	1.4
3	15	6	8.1	7.8
3	1	7	23.7	24.8
3	2	7	7.5	7.4
3	3	7	-2.1	1.3
3	4	7	3.6	3.6
3	5	7	4.0	3.6
3	6	7	7.4	7.7
3	7	7	6.7	7.8
3	8	7	8.3	8.4
3	9	7	7.2	6.5
3	10	7	5.0	4.7
3	11	7	4.1	3.9
3	12	7	5.0	5.8
3	13	7	5.3	5.2
3	14	7	4.5	3.5
3	15	7	7.6	8.8
3	0	8	12.6	13.6
3	1	8	14.5	15.0
3	2	8	-2.1	0.9
3	3	8	6.2	5.8
3	4	8	2.6	3.1
3	5	8	2.9	2.8
3	6	8	2.6	3.0
3	7	8	12.1	13.8
3	8	8	3.0	4.2
3	9	8	-2.0	1.5
3	10	8	-1.9	0.3
3	11	8	3.0	1.8
3	12	8	-1.5	0.3
3	13	8	6.1	5.1
3	14	8	-0.9	0.5
3	1	9	12.4	13.7
3	2	9	3.9	3.7
3	3	9	11.4	12.3
3	4	9	-2.1	0.4
3	5	9	-2.1	1.2
3	6	9	6.6	5.5
3	7	9	10.2	9.8
3	8	9	4.2	3.6
3	9	9	5.8	5.6
3	10	9	-1.8	0.7
3	11	9	3.2	3.0
3	12	9	3.5	2.6
3	13	9	-0.9	1.3
3	0	10	2.5	1.7
3	1	10	5.5	5.1
3	2	10	3.0	2.8
3	3	10	5.9	5.4
3	4	10	8.1	8.2
3	5	10	7.0	6.5
3	6	10	-1.9	0.8
3	7	10	2.6	3.4
3	8	10	-1.8	1.5
3	9	10	1.5	1.7
3	10	10	-1.3	0.8
3	11	10	-1.1	1.3
3	1	11	3.2	3.4
3	2	11	-1.9	0.6
3	3	11	-1.9	0.4
3	4	11	2.7	2.1
3	5	11	-1.8	0.2
3	6	11	-1.7	0.7
3	7	11	5.8	4.4
3	8	11	-1.3	1.8
3	9	11	-1.1	1.2
3	10	11	2.7	3.3
3	0	12	2.0	2.1
3	1	12	5.0	4.7
3	2	12	-1.5	0.3
3	3	12	5.6	5.2
3	4	12	2.5	1.9
3	5	12	1.6	1.2
3	6	12	2.1	2.6
3	7	12	1.5	1.3
3	8	12	-0.7	2.8
3	1	13	2.9	3.4
3	2	13	-1.0	0.0
3	3	13	3.5	4.2
3	4	13	-0.9	0.4
4	2	0	10.6	7.7
4	4	0	3.4	2.9
4	6	0	4.9	3.0
4	8	0	12.9	12.8
4	10	0	10.5	10.1
4	12	0	3.2	2.9
4	14	0	6.1	5.7
4	16	0	2.5	2.8
4	1	1	11.2	12.5
4	2	1	8.1	8.2
4	3	1	4.5	4.6
4	4	1	23.9	22.5
4	5	1	5.8	5.5
4	6	1	4.5	3.7
4	7	1	5.5	5.6
4	8	1	5.4	5.2
4	9	1	12.4	11.8
4	10	1	7.7	7.7
4	11	1	3.7	3.1
4	12	1	19.8	17.6
4	13	1	-1.3	0.0
4	14	1	3.1	2.6
4	15	1	3.4	3.2
4	16	1	2.2	2.1
4	0	2	11.7	13.7
4	1	2	3.5	3.8
4	2	2	7.9	7.9
4	3	2	18.4	18.2
4	4	2	3.7	4.1
4	5	2	17.8	17.7
4	6	2	2.7	2.8
4	7	2	6.0	5.9
4	8	2	5.5	5.1
4	9	2	5.3	5.4
4	10	2	21.4	21.2
4	11	2	12.3	12.2
4	12	2	1.4	1.3
4	13	2	6.2	5.7
4	14	2	2.8	3.0
4	15	2	4.6	4.0
4	16	2	-0.6	0.8
4	1	3	4.9	5.0
4	2	3	12.8	13.5
4	3	3	6.1	5.5
4	4	3	4.4	3.4
4	5	3	2.0	1.1
4	6	3	8.0	8.6
4	7	3	2.4	2.2
4	8	3	7.1	8.3
4	9	3	15.0	14.6
4	10	3	7.6	7.4
4	11	3	4.0	3.6
4	12	3	-1.3	0.4
4	13	3	2.9	2.6
4	14	3	-1.1	0.4
4	15	3	1.6	1.4
4	0	4	3.7	3.8
4	1	4	2.1	1.6
4	2	4	6.0	4.6
4	3	4	9.5	9.9
4	4	4	2.8	1.0
4	5	4	9.9	10.5
4	6	4	6.5	6.1
4	7	4	-1.4	0.9
4	8	4	-1.4	0.7
4	9	4	3.0	2.6
4	10	4	11.2	10.1
4	11	4	-1.4	0.1
4	12	4	-1.3	0.3
4	13	4	8.7	7.4
4	14	4	5.4	5.2
4	15	4	1.0	0.5
4	1	5	20.2	23.9
4	2	5	1.8	0.3
4	3	5	4.4	4.1
4	4	5	6.6	6.3
4	5	5	10.4	11.8
4	6	5	-1.4	0.6
4	7	5	2.1	2.6
4	8	5	2.3	1.5
4	9	5	2.2	2.4
4	10	5	1.7	1.9
4	11	5	3.4	3.0
4	12	5	4.5	4.3
4	13	5	2.5	2.2
4	14	5	4.2	3.3
4	15	5	-0.4	6.1
4	0	6	31.5	39.4
4	1	6	2.2	2.5
4	2	6	9.5	10.7
4	3	6	-1.4	0.4
4	4	6	2.3	2.9
4	5	6	8.7	9.8
4	6	6	3.7	4.0
4	7	6	5.4	5.8
4	8	6	17.3	18.3
4	9	6	2.8	2.7
4	10	6	5.0	5.5
4	11	6	3.2	2.9
4	12	6	2.6	2.2
4	13	6	5.1	4.2
4	14	6	3.1	3.1
4	1	7	-1.4	1.3
4	2	7	5.5	5.7
4	3	7	2.2	1.9
4	4	7	-1.5	0.2
4	5	7	2.5	2.8
4	6	7	7.0	7.4
4	7	7	4.2	4.5
4	8	7	2.1	1.8
4	9	7	3.1	2.9
4	10	7	-1.2	0.5
4	11	7	3.4	3.4
4	12	7	1.6	1.0
4	13	7	0.9	0.7
4	0	8	10.8	13.4
4	1	8	4.9	6.1
4	2	8	3.0	2.4
4	3	8	-1.4	0.4
4	4	8	8.3	10.2
4	5	8	7.3	8.3
4	6	8	2.3	2.4
4	7	8	2.8	3.0
4	8	8	4.6	4.6
4	9	8	2.0	1.9
4	10	8	1.5	1.5
4	11	8	-0.9	0.2
4	12	8	1.2	1.7
4	1	9	11.6	13.8
4	2	9	4.5	5.3
4	3	9	5.4	6.1
4	4	9	1.9	1.8
4	5	9	3.1	3.1
4	6	9	5.9	7.3
4	7	9	4.3	4.2
4	8	9	-1.1	1.1
4	9	9	-1.0	0.2
4	10	9	3.4	3.4
4	11	9	-0.6	0.3
4	0	10	6.6	7.5
4	1	10	1.5	0.7
4	2	10	3.0	2.7
4	3	10	2.3	1.8
4	4	10	1.6	1.5
4	5	10	1.9	2.0
4	6	10	1.5	2.7
4	7	10	4.4	4.2
4	8	10	1.0	0.8
4	9	10	2.5	2.8
4	1	11	2.2	2.4
4	2	11	2.3	2.8
4	3	11	2.5	2.8
4	4	11	3.7	3.4
4	5	11	1.8	1.7
4	6	11	1.1	0.9
4	7	11	1.0	0.5
4	0	12	1.0	5.4
4	1	12	1.8	1.3
4	2	12	3.2	2.2
4	3	12	0.6	0.9

tors were calculated by the five-parameter equation of Moore (1963), using his values for the parameters of oxygen, nitrogen, carbon (valence), and hydrogen. Individual isotropic temperature parameters were used initially for all included atoms. When the discrepancy index, R, had fallen to 0·136, anisotropic thermal parameters were applied to the heavy atoms, and the four hydrogen atoms, modified by isotropic thermal parameters, were introduced into the least-squares calculations. The initial positions of the hydrogen atoms were obtained from a three-dimensional difference Fourier synthesis. Also, 11 reflections which were suspected of suffering from secondary extinction were assigned zero weights. These are indicated by an asterisk in Table 1, which lists the observed and calculated structure amplitudes. It was found that the isotropic thermal parameters of the hydrogen atoms did not refine, and so they were kept at fixed values; the hydrogen positional parameters did refine, however. When R reached a value of 0·071, no further improvement occurred and the refinement was terminated. The final parameters for all atoms, based on the 721 reflections with nonzero weights, are listed in Table 2. The standard deviations given were calculated from the weighted residuals and the diagonal elements of the inverted matrix of the final least-squares cycle.

The layer-line scale factors were calculated by comparing the calculated and experimental structure amplitudes of those reflections included in the least-squares calculation. New scale factors were calculated at the completion of each least-squares cycle.

Discussion

The crystal structure of TNX (Fig. 1) was found to be isomorphous with the structure reported for 1,3-dichloro-2,4,6-trinitrobenzene by Holden & Dickinson (1967). Details of the two structures are remarkably similar. The precision obtained for TNX is somewhat better than that found by Holden & Dickinson for the chlorine compound, because of the absence of heavy atoms and the use of more reflection data.

Table 3 lists the intramolecular interatomic distances and angles and their standard deviations. They are quite comparable with those reported for other nitrobenzene derivatives whose structures have been determined recently by three-dimensional methods (see references given by Cady, 1967). Thus, the average lengths of chemically equivalent bonds are: nitrogen–oxygen, 1·218 Å; nitrogen–carbon (ar), 1·477 Å; and carbon (ar)–carbon (ar), 1·384 Å. Some bonds of this last type deviate from the average by 0·010 Å. While this variation is not clearly significant in itself, it appears to be significant in view of the similar results reported by Cady (1967) for *N*-methyl-*N*,2,4,6-tetranitroaniline, Grant & Richards (1969) for 3,5-dinitro-4-methylbenzoic acid and Gramaccioli, Destro & Simonetta (1968) for 2,4,6-trinitrophenetole. The carbon (ar)–carbon (al) distance of 1·495 Å is slightly shorter than similar bonds found in related compounds: 1·511 Å in *N*,3-dimethyl-4-bromo-2,6-dinitroaniline (Abrahamson, Innes & Lamm, 1967), 1·509 Å in nitromesitylene (Trotter, 1959) and 1·518 Å in 3,5-dinitro-4-methylbenzoic acid. The differences are two to three times the standard deviation of this

Table 3. *Bond lengths and bond angles in TNX*

Numbers in parentheses are standard deviations.

O(1)–N(1)	1·220 (0·004) Å.	O(1)–N(1)–O(2)	125·1 (0·3)°
O(2)–N(1)	1·223 (0·004)	O(1)–N(1)–C(2)	116·7 (0·3)
O(3)–N(2)	1·212 (0·004)	O(2)–N(1)–C(2)	118·2 (0·2)
N(1)–C(2)	1·475 (0·004)	O(3)–N(2)–O(3′)	125·2 (0·3)
N(2)–C(5)	1·480 (0·004)	O(3)–N(2)–C(5)	117·4 (0·2)
C(1)–C(2)	1·394 (0·004)	C(1)–C(5)–C(1′)	127·2 (0·3)
C(1)–C(5)	1·384 (0·004)	C(2)–C(1)–C(5)	114·2 (0·3)
C(2)–C(4)	1·374 (0·004)	C(1)–C(2)–C(4)	122·4 (0·3)
C(1)–C(3)	1·495 (0·005)	C(2)–C(4)–C(2′)	119·5 (0·3)
		C(3)–C(1)–C(2)	124·6 (0·3)
		C(3)–C(1)–C(5)	121·1 (0·2)
		N(1)–C(2)–C(1)	120·8 (0·3)
		N(1)–C(2)–C(4)	116·7 (0·2)
		N(2)–C(5)–C(1)	116·4 (0·2)

Table 2. *Final atomic parameters and their standard deviations*

The anisotropic thermal parameters are of the form: $T = \exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right]$ and are $\times 10^4$.

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0·2498 (4)	0·3622 (2)	0·0728 (2)	388 (11)	30 (1)	89 (2)	−40 (4)	−58 (7)	36 (3)
O(2)	0·5166 (4)	0·2617 (2)	0·0979 (2)	322 (12)	42 (1)	101 (3)	−10 (6)	73 (7)	12 (3)
O(3)	−0·1590 (6)	−0·0323 (2)	0·1999 (3)	491 (14)	31 (1)	112 (3)	−73 (5)	18 (9)	−29 (3)
N(1)	0·3193 (6)	0·2909 (2)	0·1107 (2)	331 (14)	27 (1)	58 (2)	−39 (5)	−35 (7)	3 (2)
N(2)	0	0·0049 (2)	$\frac{1}{4}$	326 (15)	24 (1)	68 (3)	0	80 (10)	0
C(1)	0·1563 (6)	0·1446 (2)	0·1749 (3)	296 (14)	26 (1)	56 (2)	3 (5)	−27 (7)	0 (2)
C(2)	0·1518 (6)	0·2375 (2)	0·1792 (2)	248 (12)	26 (1)	55 (2)	−16 (5)	−23 (6)	5 (2)
C(3)	0·3038 (8)	0·0912 (2)	0·0926 (3)	367 (17)	30 (1)	73 (3)	−6 (6)	57 (10)	0 (3)
C(4)	0	0·2837 (3)	$\frac{1}{4}$	236 (17)	22 (1)	68 (3)	0	−35 (10)	0
C(5)	0	0·1036 (2)	$\frac{1}{4}$	406 (20)	17 (2)	59 (4)	0	−7 (11)	0
H(1)	0·223 (8)	0·044 (4)	0·061 (5)	3·65*					
H(2)	0·467 (9)	0·080 (3)	0·123 (5)	3·65*					
H(3)	0·350 (9)	0·119 (3)	0·023 (5)	3·65*					
H(4)	0	0·337 (5)	$\frac{1}{4}$	3·65*					

* These values are not $\times 10^4$.

bond length and thus may be significant. The carbon-hydrogen bond lengths in the methyl group range from 0·92 to 1·01 (±0·05 Å); the ring C–H bond is 0·80 Å. The bond angles involving hydrogen in the methyl group range from 96 to 118 (±4°).

It has been observed that the bond angles at carbon atoms having nitro groups as substituents are significantly larger than those of carbon atoms having hydrogen atoms as substituents (Carter, McPhail & Sim, 1966). This effect has been explained (Bent, 1961) by the strong electron-attracting power of the nitro group reducing the *s* character of the carbon σ orbital to the nitrogen atom, and increasing the *s* character of the carbon σ orbitals to the adjacent carbon atoms, thus causing the bond angles to be greater than 120°. In agreement with these observations, the nitro-substituted carbon atoms in TNX have C–C–C bond angles of 122·4° at C(2) and 127·2° at C(5). The methyl-substituted ring atoms have C–C–C bond angles of 114·2°, considerably less than 120°, while the bond angle at the hydrogen-substituted atoms is 119·5°

Table 4 gives the least-squares equations of some atomic planes in the TNX molecule. The benzene ring is planar to well within the precision of the analysis. The methyl carbon atom C(3) and N(1) deviate significantly from this plane, presumably due to packing requirements. The nitro group between the two methyl groups is rotated 75·2° out of the plane of the ring, while the other nitro group with only one adjacent methyl group is rotated 35·7°. Similar angles of twist were observed in 1,3-dichloro-2,4,6-trinitrobenzene (Holden & Dickinson, 1967). A survey of the structures of a number of aromatic nitro compounds in which the nitro groups are not involved in hydrogen-bonding shows that nitro groups with no adjacent substituents (other than hydrogen) are twisted an average of 5° from the plane of the benzene ring, those with one adjacent substituent are twisted about 40°, and those with two adjacent substituents are twisted about 70°.

Table 4. *Equations of least-squares planes*

Coordinates are in Å.

Plane		
1	Benzene ring:	$0{\cdot}6846X+0{\cdot}0001Y+0{\cdot}7289Z=2{\cdot}074$ Å
2	Nitro group I:	$0{\cdot}2810X+0{\cdot}4469Y+0{\cdot}8493Z=3{\cdot}534$
3	Nitro group II:	$-0{\cdot}5299X+0{\cdot}0000Y+0{\cdot}8481Z=2{\cdot}413$

Angles between planes

Planes	
1–2	35·7°
1–3	75·2

Deviations of atoms from the plane of the benzene ring:

Atoms defining plane	C(1)	−0·009 Å
	C(1′)	0·009
	C(2)	0·009
	C(2′)	−0·009
	C(4)	0·000
	C(5)	0·000
Other atoms	N(1)	0·099
	N(2)	0·000
	C(3)	−0·112

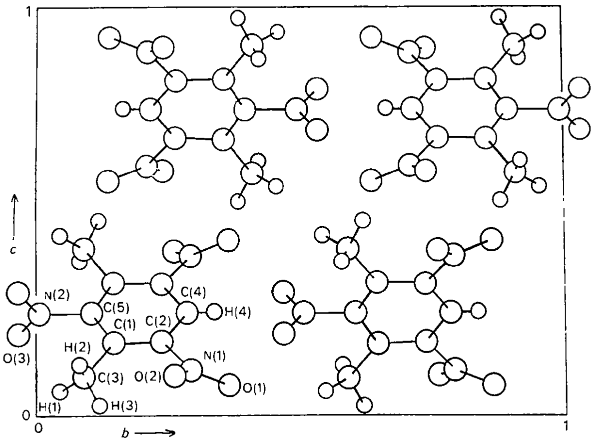

Fig. 1. Schematic drawing of the crystal structure of 2,4,6-trinitro-*m*-xylene, showing the numbering of the atoms. The contents of one unit cell are depicted.

The shortest intramolecular approaches between oxygen and hydrogen atoms are 2·49 Å [O(2)–H(3)] and 2·50 Å [O(1)–H(4)]. The shortest distances involving O(3) are 2·94 Å to H(1) and 3·17 Å between H(2) and O(3′). These longer distances for O(3) suggest that molecular packing may play as important a role in determining the angle of rotation of this nitro group from the plane of the benzene ring (75·2°) as does the proximity of the two methyl groups.

The conformation of the molecules should preclude significant interactions between the benzene rings. All short intermolecular contacts involve nitro groups. These are of three kinds: O(1)–O(2′) $(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$, 3·004 Å; O(2)–N(1″) $(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$, 3·047 Å; and O(1)–O(3″) $(\frac{1}{2}-x,\frac{1}{2}+y,z)$, 3·181 Å. Each occurs four times per molecule, making a total of 12 short contacts. These distances are similar to those found in other trinitro compounds, *e.g.* 2,4,6-trinitrophenetole (Gramaccioli *et al.*, 1968).

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