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A Direct Determination of the Crystal Structure of 2,3,4,6-Tetranitroaniline

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The symbolic addition procedure has been used to determine the crystal structure of 2,3,4,6-tetranitroaniline, $C_6H_3N_5O_8$. The crystals are monoclinic in space group $P2_1/c$ with $a_0=7{\cdot}27$, $b_0=11{\cdot}06$, $c_0=12{\cdot}27$ Å and $\beta=98°47'$. The calculated density is 1·86 g.cm^{-3} with 4 molecules in the unit cell. The measured density is 1·87 g.cm^{-3}. The structure was refined, by both Fourier and full-matrix least-squares techniques, to a final R value of 0·08. The carbon–carbon bonds in the benzene ring are not 1·40 Å. Those at the amine group carbon average 1·43 Å and the remainder 1·37 Å. The molecule as a whole is not planar; the nitro groups at C(2), C(3) and C(4) are found to be rotated by 45°, 64° and 19° respectively out of the best plane through the benzene ring.

Introduction

It has been observed that poly-substituted aromatic compounds exhibit distortion of the aromatic nucleus, unusual exocyclic bond lengths, inter- and intramolecular hydrogen bonding, and crowding of substituent groups. Cady & Larson (1965) have reported that 1,3,5-triamino-2,4,6-trinitrobenzene exhibits carbon–carbon bond lengths that average nearly 1·45 Å. Holden (1962) has reported for 1,3-diamino-2,4,6-trinitrobenzene carbon–nitrogen bond lengths of 1·40 Å at C(2) and 1·48 Å at C(6). Both of these molecules form strong hydrogen bond networks, 1,3,5-triamino-2,4,6-trinitrobenzene bonding into sheets and 1,3-diamino-2,4,6-trinitrobenzene into chains with only weak interactions between chains. Gafner & Herbstein (1962) and Ferguson & Sim (1962), among others, have published several papers concerning the effects of overcrowding on aromatic systems.

The structure of 2,3,4,6-tetranitroaniline (TENA) was undertaken to study these phenomena further because of the many possibilities offered by the functional groups present. Vicinal nitro groups are large enough to cause overcrowding and the system as a whole has the possibility of a large degree of conjugation. Because amine groups may act as donors and nitro groups as receptors, the possibilities of inter- and intramolecular hydrogen bonding also exist. Further, since no two nitro groups have the same pair of nearest neighbors, the molecule provides an opportunity for study of the effect of various environments on the configuration of a nitro group. Finally, Flürscheim (1921) has reported enhanced reactivity of the nitro group at C(3) toward certain nucleophiles and it was hoped that this reactivity might be reflected in some feature of the structure.

Determination of the structure

Experimental

A sample of the material was obtained from the Organic Chemistry Division of the U.S. Naval Ordnance Laboratory and suitable crystals were grown without purification by slowly cooling a benzene–acetone solution. The crystal used in the collection of the data was a triangular plate broken from a larger, lath-shaped crystal. This crystal fragment was approximately 0·3 mm in its largest dimension. The linear absorption coefficient for TENA is 15·92 cm^{-1} for Cu $K\alpha$ radiation. No absorption or extinction corrections were applied. The intensity data were collected at room temperature with the crystal rotating about the b axis upon a non-integrating Weissenberg camera using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The reflection intensities were visually estimated using a gray scale prepared from a typical reflection from the same crystal that was used to collect the intensity data. The range of measured intensities was 7 to 41,000 on an arbitrary scale. The number of reflections in the region of reciprocal space measured was 1690 of which 1074 were of detectable intensity.

Crystallographic data

Precession, Weissenberg and oscillation films were used to obtain the crystallographic data for TENA. From these techniques the following data were obtained:

Cell dimensions:

$$a_0=7{\cdot}27\pm0{\cdot}01,\ b_0=11{\cdot}06\pm0{\cdot}02,\ c_0=12{\cdot}27\pm0{\cdot}02\ \text{Å}$$
$$\beta=98{\cdot}8°\pm0{\cdot}3$$

Cell volume: 972 Å^3.

Density: observed, 1·87 g.cm^{-3}; calculated, 1·86 g.cm^{-3} with $Z=4$. Systematic absences: $h0l$; $l=2n+1$; $0k0$; $k=2n+1$.

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From these periodic absences on the precession and Weissenberg films the space group was uniquely determined as $P2_1/c$. $F(000)$ is 552.

Trial structure

The visual estimates of intensity were averaged, greater weight being given to those measurements in the mid-region of the intensity range, and 1/Lp corrections were applied with the use of a crystallographic computing system, X-ray 63 (Stewart *et al.*, 1964). After trying unsuccessfully to obtain a trial structure through interpretation of the Patterson function we turned to the symbolic addition procedure (Karle & Karle, 1963), which had been successfully applied to several centrosymmetric structures. The first step in this procedure was the conversion of the intensity data to a set of quasi-normalized structure factors, E values (Hauptman & Karle, 1953). The method of conversion was that developed for the X-ray 63 computing system. The atomic scattering factors used in this and all other calculations were those tabulated by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen and oxygen. The atomic scattering factors used for hydrogen were those of McWeeny (1951).

E values may be defined as follows:

$$E(hkl)=KF(hkl)\exp\left[B(\sin\theta(hkl)/\lambda)^x\right]/\left[\varepsilon\sum_{j=1}^{N}f^2(j)n(j)\right]^{\frac{1}{2}}$$

where

K = scale constant
$F(hkl)$ = relative structure factor
B = overall temperature factor
$\theta(hkl)$ = Bragg angle
λ = X-ray wavelength
x = temperature factor exponent (assumed = 2 for TENA)
ε = systematic extinction compensation weight
$f(j)$ = form factor of atom j
$n(j)$ = number of atoms of type j in the cell
N = number of atom types in the cell.

Values of K and B are determined by the conversion program. In this calculation, for each value of B the value of K is set so that the average value of E^2 is 1·0 and the value of B is adjusted by trial and error so as to minimize the resulting sum of $(E^2-1)^2$. This has the desired effect of producing a set of quasi-normalized structure factors whose magnitudes tend to show no trend with increasing diffraction angle. These values then constitute a proper set of E values.

The principal advantage of estimating E values by this method is that the data need not be divided into arbitrary groups, but rather may be treated *in toto*. This method, in addition to giving good E values, is a very direct way to estimate temperature and scale factors. The E values are used in the symbolic addition procedure, while $\varepsilon(E)^2$ and $\varepsilon(E)^2-1$ serve as coefficients for producing sharpened and sharpened, origin-removed Patterson functions.

The symbolic addition procedure was carried out with only those reflections with E values greater than 1·5. An origin was defined by assigning the 612, the 25$\bar{5}$ and the 368 reflections a phase of 0°, and then using the Σ_2 relationship to assign phases to related reflections. In order to obtain enough phase relationships, it was found necessary to assign the 13$\bar{3}$, the 240 and the 645 reflections phase cosines of a, b and c respectively. Because of relationships that developed during the application of the symbolic addition procedure it was possible to assign b a value of -1 and c a value of $+1$. The symbol a was not determined and both the $+1$ and -1 values were used in subsequently calculated E maps. Of the 114 phases assigned consistent with an a value of $+1$, 5 were incorrect as shown by the final structure.

E maps, Fourier maps calculated with the quasi-normalized structure factors as coefficients, were calculated for both possible a phase values using these 114 reflections. The 19 largest peaks were selected from each map and refinement begun on both structures.

Preliminary refinement

During the early stages of refinement Fourier methods were employed. Nitrogen atoms, as a compromise between carbon, nitrogen and oxygen atoms, were placed at each indicated atomic position, the electron density calculated at 27 points about each position and the atom moved to coincide with the interpolated position of maximum electron density. Both possible structures were refined by several cycles of this procedure. One structure refined from an R of 0·59 to an R of 0·53, and the other structure from an R of 0·52 to an R of 0·37. A difference Fourier synthesis calculated for this second structure clearly indicated which atoms were carbon, which nitrogen and which oxygen. The atoms were placed as indicated and Fourier refinement continued, several cycles reducing R to 0·19.

Final refinement

Several cycles of full-matrix least squares were run, using individual isotropic temperature factors and level by level scale factors, minimizing $\Sigma\, w(\Delta F^2)$. This isotropic refinement reduced R from 0·19 to 0·13. Several more cycles were run with individual anisotropic temperature factors for all non-hydrogen atoms and a Hughes type weighting scheme (Hughes, 1941). The 12$\bar{2}$, 22$\bar{1}$, 13$\bar{3}$, 042 and 240 reflections were given zero weight. The remaining reflections were divided into two clases for weighting purposes. The observed reflections were weighted as follows:

$$w=10/F_{\text{rel}}\qquad F_{\text{rel}}\geq 10,$$
$$w=1{\cdot}0\qquad F_{\text{rel}}<10.$$

Unobserved reflections were weighted

$$w=1{\cdot}0\qquad F_c>F_{\text{min}},$$
$$w=0{\cdot}0\qquad F_c\leq F_{\text{min}},$$

Table 1. *Final atomic parameters*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·7532 (5)	0·3357 (3)	0·2208 (3)	3·0 (1)	2·7 (2)	4·3 (2)	−0·3 (1)	0·3 (1)	0·2 (1)
C(2)	0·5893 (5)	0·4094 (4)	0·2004 (3)	3·7 (2)	2·0 (2)	4·3 (2)	−0·1 (1)	0·8 (1)	0·1 (1)
C(3)	0·4453 (5)	0·3834 (4)	0·1192 (3)	2·6 (1)	3·2 (2)	4·0 (2)	−0·1 (1)	0·6 (1)	0·4 (1)
C(4)	0·4541 (5)	0·2841 (4)	0·0515 (3)	3·6 (2)	3·1 (2)	4·0 (2)	−0·4 (1)	0·2 (1)	0·1 (1)
C(5)	0·6127 (6)	0·2143 (4)	0·0623 (3)	4·4 (1)	2·8 (2)	3·9 (2)	−0·1 (1)	0·5 (1)	0·2 (1)
C(6)	0·7587 (5)	0·2401 (3)	0·1431 (3)	3·4 (2)	2·4 (2)	4·2 (2)	0·1 (1)	0·6 (1)	−0·1 (1)
N(1)	0·8867 (5)	0·3577 (4)	0·3031 (3)	3·9 (1)	3·8 (2)	4·9 (2)	0·6 (1)	−0·5 (1)	−0·9 (1)
N(2)	0·5837 (5)	0·5209 (3)	0·2646 (3)	3·6 (1)	2·7 (2)	5·1 (2)	0·1 (1)	1·0 (1)	−0·1 (1)
N(3)	0·2815 (5)	0·4655 (3)	0·1039 (3)	3·5 (1)	3·6 (2)	5·0 (2)	0·3 (1)	0·8 (1)	0·8 (1)
N(4)	0·2953 (5)	0·2434 (4)	−0·0254 (3)	4·6 (2)	3·9 (2)	4·6 (2)	−1·0 (1)	−0·4 (1)	0·2 (1)
N(6)	0·9187 (5)	0·1591 (3)	0·1489 (3)	4·1 (2)	2·7 (2)	5·5 (2)	0·2 (1)	0·9 (1)	0·0 (1)
O(21)	0·6364 (4)	0·5170 (3)	0·3636 (2)	5·2 (1)	3·8 (2)	4·6 (2)	0·3 (1)	0·5 (1)	−0·8 (1)
O(22)	0·5262 (5)	0·6118 (3)	0·2146 (3)	6·5 (2)	2·7 (2)	6·6 (2)	0·8 (1)	1·2 (1)	0·1 (1)
O(31)	0·1903 (4)	0·4682 (4)	0·1786 (3)	4·7 (2)	7·1 (2)	6·7 (2)	1·6 (1)	2·4 (1)	1·3 (2)
O(32)	0·2551 (5)	0·5215 (3)	0·0185 (3)	4·8 (1)	5·2 (2)	6·2 (2)	1·0 (1)	0·5 (1)	2·2 (1)
O(41)	0·1419 (4)	0·2826 (4)	−0·0150 (3)	3·7 (1)	6·8 (2)	7·6 (2)	−0·6 (1)	−0·6 (1)	−0·2 (2)
O(42)	0·3225 (5)	0·1718 (4)	−0·0977 (3)	6·6 (2)	5·6 (2)	5·5 (2)	−0·7 (1)	−0·8 (1)	−1·4 (1)
O(61)	0·9133 (5)	0·0794 (3)	0·0795 (3)	6·0 (2)	3·2 (2)	6·7 (2)	0·9 (1)	0·5 (1)	−1·4 (1)
O(62)	1·0504 (4)	0·1752 (3)	0·2211 (3)	4·3 (1)	4·8 (2)	6·8 (2)	1·3 (1)	−0·4 (1)	−0·9 (1)
H(5)	0·6125 (72)	0·1431 (51)	0·0098 (41)	4·3*					
H(11)	0·9919 (77)	0·3028 (56)	0·3157 (43)	4·3*					
H(12)	0·8721 (74)	0·4194 (59)	0·3555 (45)	4·3*					

* Isotropic temperature factor used for hydrogen atoms and never refined.

where $F_{\min}$ is F_{rel} calculated from the minimum observed intensity. The final parameters are shown in Table 1. The anisotropic temperature factors are defined by the following equation:

$$\text{T.F.} = \exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33} + 2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})\right].$$

These B_{ij} values are on the same scale as the overall isotropic B in the expression:

$$F_o = F_c \exp\left(-B\sin^2\theta/\lambda^2\right).$$

The errors, which are in the last place or last two places, are given in parentheses. The agreement factors from the last least-squares cycle are found in Table 2, and the structure factors in Table 3.

Table 2. *Values from final least-squares cycle*

$\Sigma\, w(\Delta F)^2$	665
$[\Sigma\, w(\Delta F)^2/(\text{NO}-\text{NV})]^{\frac{1}{2}}$	0·66
R, omitting unobserveds	0·081
R, with reflection multiplicity omitting unobserveds	0·081
Weighted R value, omitting unobserveds	0·104
R value of unobserveds calculating greater than intensity minimum	0·057
Number of unobserveds calculating greater than intensity minimum	84 of 616
Total number of observations (NO)	1690
Total number of variables (NV)	190

Hydrogen atoms

The hydrogen atoms were located from difference syntheses and their positions refined by full-matrix least-squares along with the other parameters. The hydrogen atoms were assigned an isotropic temperature factor which was not refined. The value chosen was that indicated for the overall B by the calculation of quasi-normalized structure factors. The atomic positions of the hydrogen atoms were quite stable, no damping or resetting being necessary.

Scale factors

Level scale factors, where each level is that group of reflections with constant index k, were used throughout. No cross reference exposures were used, but an effort was made to keep the data on the same scale by exposing all of the film packs for the same length of time, at the same current and voltage and developing them in the same manner. A first approximation of the value of an overall scale factor was obtained from the calculation of quasi-normalized structure factors by the method described above.

The overall scale factor was used during Fourier refinement and as the starting value for the least-squares refinement. The values of the level scale factors were refined only during the first cycles of least-squares refinement along with individual isotropic atomic temperature factors. No further refinement of the scale factors was attempted during refinement with anisotropic temperature factors because of the high correlation between the scale factors and the B_{22} temperature factors.

The final level scale factors obtained in this way show no trend with k and the values of the B_{22} are not noticeably different from the B_{11} and B_{33} values.

Lingafelter & Donohue (1966) have pointed out that refinement of level scale factors along one crystallographic direction is undesirable because it increases the standard deviation of the positional and thermal parameters associated with that direction.

Discussion

The final atomic parameters and the errors indicated by the inverse matrix from the final least-squares refinement are given in Table 1. The bond lengths and angles are given in Figs. 1 and 2, respectively. The average error in the non-hydrogen bond distances is 0·006 Å and in the angles 0·38°. The largest error in each case is 0·007 Å and 0·44°. The equation of the best plane through the six carbon atoms of the ring as determined by the method of Schomaker, Waser, Marsh & Bergman (1959) is

$$-3{\cdot}681x-6{\cdot}547y+8{\cdot}550z=-3{\cdot}118$$

and $\sigma=0{\cdot}024$ Å. The deviations of the atoms from this plane appear in Table 4.

The carbon–carbon bond lengths are similar to those reported for 1,3-diamino-2,4,6-trinitrobenzene (Holden, 1962) and 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965). Bonds C(1)–C(2) and C(6)–C(1), the bonds involving the carbon atom with the amine substituent, are significantly longer than the normal 1·397 Å reported for benzene (Langseth & Stoicheff, 1956), averaging 1·431 Å. The remaining four

Table 3. *Observed and calculated structure factors*

The table contains l, $10|F_o|$ and $10F_c$. Reflections tagged L are unobserved and $|F_{\min}|$ is given for $|F_o|$. Reflections marked E have weight 0·0.

0,0,L		
2	190	-224
4	108	125
6	23	18
8	72	76
10	59	71
12	81	-84
14	36	40
1,0,L		
0	453	-430
2	12L	-13
-2	97	-91
4	334	376
-4	383	-345
6	341	324
-6	145	165
8	70	-79
-8	56	-57
10	41	36
-10	28L	29
12	36	32
-12	160	138
14	47	40
-14	23L	-16
2,0,L		
0	132	-182
2	442	-450
-2	781	-742
4	467	404
-4	239	-241
6	576	-578
-6	165	160
8	27L	19
-8	277	-272
10	29L	29
-10	170	-161
12	100	-95
-12	33	30
14	29	28
-14	23L	-8
3,0,L		
0	18L	-15
2	142	174
-2	112	127
4	28	34
-4	497	-491
6	155	-166
-6	214	-219
8	114	120
-8	67	74
10	121	-125
-10	143	148
12	55	56
-12	63	-65
4,0,L		
0	64	-67
2	181	180
-2	315	-275
4	267	273
-4	63	-56
6	93	-101
-6	62	71
8	109	124
-8	40	-38
10	27L	-17
-10	60	62
12	19L	-6
-12	27L	-20
5,0,L		
0	136	-134
2	159	-156
-2	238	-214
4	185	-190
-4	372	330
6	42	-50
-6	98	96
8	28L	2
-8	54	-70
10	86	-71
-10	33	-21
-12	51	51
6,0,L		
0	298	-262
2	122	134
-2	36	41
4	29L	34
-4	152	-132
6	28L	-6
-6	92	104
8	24L	-24
-8	29L	-3
10	15L	-20
-10	37	29
7,0,L		
0	67	65
2	28L	-3
-2	176	173
4	89	77
-4	41	48
6	23L	-8
-6	28	-22
-8	37	44
-10	24	29
8,0,L		
0	25L	-0
2	23L	-0
-2	25L	33
4	38	42
-4	25L	19
-6	23L	-22
0,1,L		
2	636	-636
3	156	-178
4	106	121
5	400	-395
6	76	91
7	25L	-9
8	27L	26
9	78	-73
10	32L	20
11	67	-68
12	201	166
13	67	67
14	40	39
15	19L	9
1,1,L		
0	84	-96
1	278	274
-1	224	299
2	488	-560
-2	628	-584
3	370	393
-3	1053	-969
4	53	50
-4	442	-434
5	91	91
-5	90	87
6	90	86
-6	59	-61
7	150	-157
-7	253	-260
8	28L	-13
-8	182	-200
9	31L	-1
-9	120	112
10	99	-98
-10	36	-46
11	32L	24
-11	32L	6
12	31L	-3
-12	32	-34
13	40	36
-13	114	-102
14	23L	-2
-14	136	118
-15	39	25
2,1,L		
0	228	318
1	808	790
-1	76	-62
2	286	-299
-2	93	95
3	49	-58
-3	164	178
4	660	-703
-4	19L	18
5	23L	26
-5	257	254
6	140	-146
-6	23L	28
7	28L	13
-7	26L	-16
8	30	-33
-8	89	89
9	65	69
-9	30L	-22
10	32L	-12
-10	32L	8
11	32L	-28
-11	104	94
12	54	-52
-12	32L	25
13	25L	7
-13	48	44
14	19L	-13
-14	25L	-27
-15	39	-41
3,1,L		
0	63	-56
1	172	-165
-1	677	674
2	247	243
-2	100	104
3	33	37
-3	574	-567
4	45	45
-4	284	-349
5	26L	-1
-5	173	167
6	81	-88
-6	187	174
7	30L	-20
-7	68	67
8	65	-77
-8	198	-192
9	32L	3
-9	31L	16
10	32L	29
-10	40	40
11	96	-86
-11	37	42
12	60	52
-12	31L	16
13	21L	-9
-13	32	27
-14	24L	-12
4,1,L		
0	30	23
1	277	-260
-1	480	-457
2	26L	-26
-2	92	96
3	145	155
-3	88	88
4	28L	24
-4	177	-172
5	92	97
-5	178	-166
6	54	47
-6	32	33
7	61	-56
-7	135	120
8	32L	6
-8	31L	-25
9	78	-75
-9	52	-63
10	85	-83
-10	32L	1
11	26L	16
-11	32L	34
12	21L	-8
-12	30L	-5
-13	26L	-24
-14	22L	4
5,1,L		
0	32	39
1	62	-52
-1	36	-22
2	30L	-34
-2	176	161
3	331	301
-3	150	-159
4	31	-29
-4	60	-58
5	114	-121
-5	30L	32
6	32L	-19
-6	256	235
7	46	36
-7	32L	26
8	63	64
-8	37	38
9	91	75
-9	32L	7
10	25L	-13
-10	32L	15
11	20L	-10
-11	76	-80
-12	44	43
-13	23L	19
6,1,L		
0	190	162
1	32L	-0
-1	76	68
2	349	336
-2	32L	-4
3	46	-54
-3	186	169
4	32L	0
-4	32L	21
5	32L	8
-5	32L	-30
6	31L	15
-6	32L	-24
7	96	83
-7	66	-68
8	26L	-0
-8	32L	31
9	22L	2
-9	83	90
10	16L	9
-10	66	-62
-11	33	30
-12	22L	15
7,1,L		
0	247	-242
1	32	-25
-1	171	-165
2	80	66
-2	32L	4
3	30L	-1
-3	76	69
4	29L	-7
-4	32L	4
5	27L	26
-5	109	108
6	45	47
-6	31L	-11
7	21L	-24
-7	38	-41
8	73	48
-8	28L	-19
-9	26L	-4
-10	23L	6
-11	20L	-8
8,1,L		
0	39	-35
1	26L	-21
-1	28	33
2	25L	11
-2	28L	-11
3	23L	-20
-3	117	-86
4	32	-29
-4	27L	5
5	40	-35
-5	27L	-5
-6	25L	-33
-7	24L	25
-8	27	-29
-9	18L	-19
9,1,L		
0	17L	-4
1	15L	-10
-1	18L	23
-2	18L	-13
-3	18L	14
-4	18L	16
-5	16L	-24
0,2,L		
2	486	-522
3	89	105
4	249	-261
5	188	-202
6	27	-37
7	34	-38
8	89	89
9	133	-139
10	78	75
11	128	112
12	30L	32
13	27L	11
14	23L	-24
1,2,L		
0	401	-351
1	16	17
-1	458	431
2	340	-349
-2	1178E	1578
3	540	-528
-3	501	402
4	199	-219
-4	78	-78
5	20L	-11
-5	60	-68
6	99	-102
-6	127	-128
7	186	175
-7	24L	-26
8	355	-331
-8	53	-55
9	109	-107
-9	72	-64
10	167	-154
-10	125	109
11	30L	14
-11	38	37
12	29L	-4
-12	30	30
13	26L	-12
-13	28L	-9
14	52	-45
-14	24L	18
2,2,L		
0	114	-133
1	145	-154
-1	1008E	909
2	188	208
-2	477	-473
3	63	-60
-3	506	-508
4	162	176
-4	194	-169
5	46	-48
-5	239	234
6	109	-116
-6	22L	10
7	84	91
-7	108	-100
8	52	-44
-8	226	211
9	38	42
-9	114	-97
10	31L	25
-10	88	-88
11	76	67
-11	38	43
12	27L	-26
-12	30	32
13	23L	-1
-13	27L	8
14	17L	21
-14	23L	18
-15	18L	42
3,2,L		
0	19L	-6
1	280	323
-1	414	444
2	416	408
-2	120	-128
3	25	29
-3	75	-91
4	33	-7
-4	79	-97
5	25L	24
-5	133	-120
6	169	170
-6	133	-124
7	66	-75
-7	60	52
8	49	61
-8	123	123
9	31	-27
-9	29L	26
10	30L	9
-10	43	-53
11	28L	-6
-11	49	-57
12	24L	28
-12	104	-92
13	19L	26
-13	26L	-8
-14	22L	9
4,2,L		
0	23L	-2
1	157	-145
-1	33	-28
2	206	207
-2	330	331
3	151	155
-3	201	-193
4	27	-33
-4	284	342
5	46	27
-5	29	-26
6	80	80
-6	63	-47
7	34	-37
-7	82	78
8	63	-68
-8	29L	5
9	30L	-0
-9	101	-105
10	38	41
-10	114	116
11	24L	-17
-11	68	70
12	19L	-3
-12	57	57
-13	24L	22
-14	20L	-38
5,2,L		
0	156	152
1	122	119
-1	27L	7
2	52	-48
-2	155	-151
3	56	-57
-3	27L	-21
4	125	124
-4	51	50
5	207	-199
-5	158	-157
6	107	114
-6	60	67
7	63	78
-7	30L	20
8	29L	24
-8	31L	6
9	26L	-2
-9	30L	-1
10	23L	-13
-10	30L	28
11	18L	-0
-11	28L	-6
-12	25L	6
-13	21L	-4
6,2,L		
0	38	-38
1	92	-100
-1	55	-53
2	120	-126
-2	38	-39
3	170	166
-3	30L	-15
4	49	-60
-4	181	-158
5	61	-57
-5	30L	-16
6	32	32
-6	56	68
7	27L	23
-7	30	31
8	53	-38
-8	30L	3
9	35	-25
-9	95	-97
10	14L	0
-10	107	-95
-11	70	79
-12	56	-59
7,2,L		
0	30L	-4
1	69	80
-1	105	-100
2	41	-42
-2	141	-127
3	28	23
-3	62	-61
4	27L	-8
-4	48	-53
5	25L	-6
-5	69	69
6	31	-25
-6	75	-84
7	19L	-6
-7	26L	1
8	14L	14
-8	26L	15
-9	39	37
-10	31	-37
-11	29	-32
8,2,L		
0	25L	-19
1	24L	-1
-1	45	-42
2	23L	18
-2	66	61
3	21L	-23
-3	124	116
4	60	-49
-4	87	74
5	16L	-17
-5	50	-53
-6	23L	27
-7	22L	22
-8	19L	0
-9	16L	1
0,3,L		
2	344	-336
3	159	177
4	103	-127
5	26L	-79
6	121	125
7	32L	18
8	35L	26
9	54	55
10	40L	-25
11	141	-131
12	99	-97
13	35L	13
14	29L	-26
1,3,L		
0	161	155
1	40	-51
-1	453	-375
2	330	303
-2	603	610
3	264	280
-3	1523E	1032
4	132	146
-4	782	754
5	108	-121
-5	449	-433
6	81	-89
-6	242	242
7	215	213
-7	109	-111
8	37L	-44
-8	35L	-26
9	114	-113
-9	38L	38

carbon–carbon bonds average 1·372 Å, shorter than the benzene value. The interior angles at the carbon atoms are also similar to those reported for other polynitro aromatic compounds. Thus the angle defined by C(6)–C(1)–C(2), where the vertex carbon does not have a nitro group or hydrogen atom substituent, is considerably less than 120°, in this case being 114°. Also the endocyclic angles of the adjacent carbon atoms, C(5)–C(6)–C(1) and C(1)–C(2)–C(3), are larger than 120°, being 123° and 122° respectively. This is seen also in the structures reported for 1,3-diamino-2,4,6-trinitrobenzene, 1,3,5-triamino-2,4,6-trinitrobenzene and 1,3-dichloro-2,4,6-trinitrobenzene (Holden, 1963).

The C–NH$_2$ carbon–nitrogen distance is 1·312 Å, about the same as reported for the polynitro aromatic amines 1,3-diamino-2,4,6-trinitrobenzene and 1,3,5-triamino-2,4,6-trinitrobenzene, but significantly shorter than the value reported for *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). The bond angles of the amine group are very close to the 120° expected for trigonal bonding of the nitrogen. However, the errors in these angles are quite large, approximately 4°, making it impossible to say with certainty that the hybridization of this nitrogen is trigonal. The carbon–nitrogen bonds of the nitro groups range from the short 1·447 Å of C(4)–N(4) to the long 1·487 Å of C(3)–

Table 3 (*cont.*)

10	133	135
-10	40L	-14
11	196	173
-11	40L	9
12	38L	31
-12	63	-65
13	33L	21
-13	36L	-32
14	26L	-25
-14	30L	-4
2,3,L		
0	451	440
1	1168	962
-1	173	-186
2	91	113
-2	130	114
3	165	162
-3	53	60
4	28	-34
-4	83	-82
5	30L	20
-5	275	-245
6	42	50
-6	421	-372
7	36L	25
-7	68	61
8	38L	22
-8	82	83
9	40L	9
-9	38L	32
10	40L	10
-10	40L	-9
11	79	81
-11	40L	39
12	50	39
-12	39L	-5
13	52	-44
-13	35L	-26
3,3,L		
0	207	227
1	475	-474
-1	26L	28
2	134	-129
-2	26L	15
3	371	-348
-3	27L	22
4	80	-89
-4	170	-185
5	49	65
-5	79	75
6	37	-36
-6	69	73
7	144	126
-7	68	78
8	40	-61
-8	127	-132
9	178	-169
-9	39L	34
10	39L	-5
-10	92	90
11	36L	14
-11	40L	-18
12	31L	1
-12	38L	-1
-13	34L	-11
-14	28L	21
4,3,L		
0	220	245
1	87	-97
-1	136	-148
2	59	72
-2	161	-166
3	195	-197
-3	32L	-18
4	59	-68
-4	61	56
5	150	157
-5	162	-156
6	40L	9
-6	46	-50
7	178	-184
-7	38	-50
8	40L	67
-8	39L	-5
9	39L	-22
-9	65	-65
10	35L	27
-10	46	-45
11	31L	2
-11	39L	-29
-12	36L	33
-13	31L	10
-14	24L	-6
5,3,L		
0	46	-50
1	193	180
-1	36L	-29
2	54	63
-2	36L	16
3	132	-136
-3	42	-52
4	220	218
-4	190	-190
5	40L	17
-5	107	-110
6	65	-69
-6	49	57
7	39L	-43
-7	65	67
8	37L	-44
-8	137	-142
9	34L	34
-9	65	79
10	29L	-24
-10	39L	-13
-11	65	-62
-12	32L	17
6,3,L		
0	101	-99
1	40	49
-1	50	59
2	90	-98
-2	109	-108
3	40L	-12
-3	82	85
4	57	-69
-4	57	-63
5	44	46
-5	40L	-19
6	37L	-40
-6	65	-70
7	49	51
-7	73	78
8	30	-33
-8	124	135
-9	37L	-26
-10	34L	46
-11	31L	8
7,3,L		
0	39L	-20
1	39L	22
-1	39L	23
2	38L	7
-2	107	109
3	37L	-32
-3	39L	26
4	35L	1
-4	39L	-24
5	32L	14
-5	70	77
6	29L	-21
-6	37L	-6
-7	36L	-13
-8	34L	-7
8,3,L		
0	32L	16
1	31L	11
-1	33L	-14
2	54	49
-2	74	-69
3	27L	19
-3	119	-103
4	24L	11
-4	39	37
-5	49	55
-6	66	59
-7	27L	6
0,4,L		
2	842E	697
3	137	-149
4	81	92
5	245	-241
6	203	206
7	78	86
8	147	152
9	29L	8
10	139	-128
11	30L	-7
12	36	29
13	25L	-11
14	20L	-10
1,4,L		
0	243	-245
1	304	286
-1	311	-281
2	263	-261
-2	185	193
3	341	-383
-3	53	-49
4	103	112
-4	73	-67
5	187	-192
-5	198	-206
6	68	85
-6	56	51
7	133	-144
-7	161	-152
8	122	124
-8	75	-85
9	231	207
-9	41	-34
10	117	107
-10	137	124
11	42	41
-11	62	62
12	27L	-6
-12	29L	-16
13	24L	2
-13	26L	1
14	18L	-23
-14	21L	-1
2,4,L		
0	973E	-753
1	163	130
-1	18	-22
2	74	78
-2	187	-172
3	216	-217
-3	33	45
4	131	-147
-4	283	246
5	68	78
-5	22	19
6	88	-104
-6	307	-284
7	158	-169
-7	186	-177
8	158	-164
-8	28L	-0
9	30L	-27
-9	91	-100
10	30L	6
-10	123	-128
11	28L	-4
-11	80	-80
12	25L	26
-12	26L	29
13	21L	7
-13	25L	32
-14	21L	1
3,4,L		
0	182	156
1	125	-130
-1	181	-147
2	120	-139
-2	20L	-2
3	23L	9
-3	291	263
4	25L	-24
-4	145	-132
5	38	42
-5	224	-211
6	28L	21
-6	36	-38
7	30L	23
-7	44	50
8	30L	-33
-8	124	138
9	30L	-25
-9	48	48
10	29L	1
-10	30L	28
11	26L	0
-11	30L	27
12	22L	13
-12	132	-119
13	15L	-23
-13	24L	34
-14	19L	18
4,4,L		
0	65	53
1	162	161
-1	212	177
2	26L	14
-2	239	196
3	90	98
-3	25	28
4	151	-157
-4	89	93
5	120	-127
-5	38	41
6	276	287
-6	159	-151
7	214	-212
-7	53	-54
8	30L	-33
-8	34	-21
9	28	25
-9	75	79
10	32	36
-10	30L	26
11	22L	-4
-11	28L	9
-12	26L	2
-13	22L	-29
5,4,L		
0	144	134
1	73	76
-1	45	-52
2	112	-109
-2	198	-182
3	30L	17
-3	73	-75
4	43	-53
-4	29L	-9
5	93	87
-5	29L	-19
6	171	-172
-6	207	195
7	29L	-0
-7	131	-126
8	27L	-14
-8	77	-77
9	24L	4
-9	143	151
10	20L	-11
-10	46	-51
-11	26L	-14
-12	23L	19
-13	18L	19
6,4,L		
0	30L	16
1	30L	-20
-1	30L	14
2	55	-63
-2	30L	24
3	30L	-7
-3	55	58
4	30L	19
-4	105	-96
5	155	150
-5	30L	32
6	27L	34
-6	30L	13
7	24L	-0
-7	30L	-23
8	21L	-43
-8	29L	-2
9	16L	5
-9	27L	-15
-10	43	47
-11	22L	8
7,4,L		
0	41	37
1	32	36
-1	47	50
2	28	33
-2	60	58
3	27L	-0
-3	74	-86
4	74	66
-4	59	65
5	23L	16
-5	45	49
6	20L	-18
-6	27L	-14
-7	33	36
-8	28	34
-9	22L	14
8,4,L		
0	31	31
1	44	-50
-1	47	46
2	32	38
-2	41	44
3	32	31
-3	80	-71
-4	88	-87
-5	68	-55
-6	21L	-9
-7	33	34
0,5,L		
2	421	-431
3	550	-563
4	38	45
5	39	-34
6	91	94
7	60	-61
8	135	139
9	79	85
10	122	127
11	79	-85
12	25L	7
13	21L	-4
14	26	29
1,5,L		
0	352	-304
1	352	-284
-1	449	-416
2	294	284
-2	23	21
3	245	282
-3	83	66
4	135	-162
-4	76	-65
5	29	-25
-5	27	-28
6	71	-81
-6	142	-152
7	130	144
-7	23L	-11
8	26L	-13
-8	25L	-0
9	122	-135
-9	33	-35
10	27L	18
-10	70	-65
11	33	23
-11	27L	-16
12	43	-46
-12	64	75
13	20L	15
-13	22L	-10
-14	17L	4
2,5,L		
0	177	-143
1	67	69
-1	187	157
2	263	263
-2	174	-142
3	287	-293
-3	21	-26
4	37	-41
-4	184	175
5	22L	-2
-5	549	542
6	332	-367
-6	155	159
7	97	-114
-7	44	42
8	38	49
-8	87	95
9	184	209
-9	27L	23
10	95	-91
-10	27L	3
11	25L	-12
-11	27L	5
12	21L	-5
-12	25L	9
3,5,L		
0	19L	5
1	118	98
-1	410	336
2	21L	-15
-2	19L	19
3	56	-64
-3	152	149
4	67	-79
-4	198	190
5	40	45
-5	26	-14
6	26L	-0
-6	368	-357
7	102	113
-7	108	-98
8	27L	19
-8	94	-90
9	76	-89
-9	44	39
10	71	75
-10	103	105
11	22L	-26
-11	26L	5
12	18L	-4
-12	24L	-10
4,5,L		
0	23L	10
1	147	-149
-1	23L	-14
2	24L	15
-2	92	-90
3	72	79
-3	27	-28
4	53	51
-4	128	131
5	30	-45
-5	79	82
6	50	56
-6	201	-221
7	69	-81
-7	114	116
8	75	-79
-8	27L	8
9	63	56
-9	70	-74
10	27	21
-10	26L	-25
11	45	40
-11	25L	1
5,5,L		
0	93	86
1	54	62
-1	98	95
2	27	-15
-2	26L	-0
3	44	46
-3	42	-39
4	31	28
-4	54	-62
5	27	-27
-5	27	-6
6	48	58
-6	109	116
7	41	38
-7	103	-124
8	53	-59
-8	121	128
9	33	28
-9	26L	-24
10	20	-21
-10	24L	15
6,5,L		
0	70	80
1	27L	-18
-1	56	61
2	27L	9
-2	50	46
3	55	59
-3	31	32
4	59	68
-4	27L	12
5	40	-40
-5	27L	-1
6	23L	1
-6	27L	-13
7	20L	8
-7	26L	-17
8	17L	-16
-8	25L	7
7,5,L		
0	25L	23
1	25	-27
-1	25	-26
2	68	-88
-2	65	-81
3	23L	-30
-3	25L	-14
4	38	47
-4	25L	-2
-5	24L	-20
-6	38	-43
0,6,L		
2	366	-328
3	18L	-15
4	21L	-7
5	44	-48
6	27L	-12
7	29L	6
8	111	115
9	72	-64
10	32L	18
11	30L	-12
12	27L	13
13	23L	21
1,6,L		
0	150	152
1	80	73
-1	91	86
2	548	-430
-2	57	-52
3	86	92
-3	85	-75
4	126	141
-4	86	94
5	176	-188
-5	44	43
6	35	40
-6	199	198
7	89	-99
-7	29	27
8	152	-151
-8	31L	18
9	32L	2
-9	95	-99
10	32L	-20
-10	52	55
11	29L	-6
-11	82	81
12	67	-60
-12	28	-27
2,6,L		
0	117	-118
1	20L	22
-1	124	125
2	21L	-22
-2	57	-47
3	48	-51
-3	21L	23
4	119	-124
-4	137	126
5	112	110
-5	68	-70
6	59	47
-6	119	122
7	229	239
-7	30	28

N(3). It is interesting to note that this longest carbon–nitrogen bond, C(3)–N(3), corresponds to the nitro group reported to have enhanced chemical reactivity (Flürscheim, 1921). Of the five nitrogen atoms attached to the ring, only N(6) is within 3σ of the best plane through the 6 carbon atoms, N(2) and N(3) being on one side of this plane and N(1) and N(4) on the other. An examination of the exocyclic carbon atom angles indicates that the nitro groups in the 4 and 6 positions have been displaced toward the relatively small hydrogen atom in the 5 position.

The nitrogen–oxygen bonds range from 1·207 to 1·227 Å. These bond lengths are shorter than those reported for 1,3,5-triamino-2,4,6-trinitrobenzene and most of those of 1,3-diamino-2,4,6-trinitrobenzene, but about the same as those reported for 1,3-dichloro-2,4,6-trinitrobenzene. The displacements of the oxygen atoms from the plane of the carbon atoms indicate that only the nitro group at C(6) is approximately coplanar with the ring, the nitro groups at C(2), C(3) and C(4) being rotated approximately 45, 64 and 19° respectively. These angles are not purely torsional, but are the dihedral angles between the plane through the six carbon atoms and the planes of the individual nitro groups. The nitro group at C(3) is twisted far enough so that the closest non-bonded interactions involve N(3) rather

Table 3 (*cont.*)

8	116	123
-8	31L	-29
9	110	113
-9	32L	21
10	30L	-27
-10	154	-156
11	27L	-25
-11	30L	20
12	23L	-18
-12	50	42
3,6,L		
0	191	187
1	61	-57
-1	117	116
2	74	-75
-2	24L	2
3	352	345
-3	244	246
4	29L	-12
-4	155	-160
5	30L	-10
-5	28L	15
6	206	-210
-6	134	121
7	59	-59
-7	76	66
8	269	231
-8	145	-154
9	70	-70
-9	103	-108
10	28L	13
-10	31L	-10
11	49	50
-11	29L	-34
4,6,L		
0	28L	-19
1	77	77
-1	264	-243
2	54	56
-2	28L	11
3	31L	-20
-3	47	-42
4	31L	39
-4	256	241
5	32L	-27
-5	179	-175
6	59	-72
-6	31L	-37
7	31L	2
-7	32L	4
8	34	-35
-8	40	-45
9	27L	24
-9	144	150
10	23	19
-10	74	83
-11	27L	-1
5,6,L		
0	32L	16
1	78	-83
-1	31L	0
2	32L	22
-2	51	52
3	79	-79
-3	32	35
4	59	63
-4	91	93
5	78	-75
-5	32L	-17
6	30	-36
-6	32	-17
7	32	33
-7	45	-55
8	25	31
-8	31L	-2
9	61	-50
-9	30L	-14
6,6,L		
0	32L	-23
1	72	78
-1	88	-103
2	31L	2
-2	82	85
3	81	-83
-3	32L	-13
4	73	-76
-4	121	-125
5	45	40
-5	31L	7
6	25L	6
-6	31L	-34
7	22L	-9
-7	29L	-26
8	17L	-8
-8	39	-39
-9	25L	0
7,6,L		
0	45	-51
1	27L	-19
-1	28L	2
2	46	38
-2	41	-46
3	25L	33
-3	32	-28
4	23L	15
-4	28L	-16
5	39	32
-5	38	48
6	55	-53
-6	26	-28
-7	24L	9
-8	21L	-16
-9	18L	-15
8,6,L		
0	43	10
1	18L	11
-1	20L	43
2	15L	-6
-2	21L	30
-3	20L	-7
0,7,L		
2	95	-101
3	127	-121
4	256	238
5	117	115
6	144	-139
7	31	36
8	59	57
9	33L	-10
10	66	-61
11	30L	-22
12	42	36
1,7,L		
0	161	-170
1	186	-164
-1	120	125
2	86	86
-2	233	230
3	45	-36
-3	20L	12
4	292	287
-4	232	211
5	27L	23
-5	125	129
6	120	114
-6	29L	16
7	78	76
-7	31L	38
8	33L	7
-8	32L	2
9	33L	7
-9	33L	4
10	31L	-11
-10	32L	-8
11	28L	33
-11	30L	-21
2,7,L		
0	66	60
1	104	99
-1	60	56
2	33	-31
-2	70	-59
3	32	35
-3	89	-84
4	28	-20
-4	194	-173
5	149	144
-5	111	104
6	45	-42
-6	30L	15
7	33L	36
-7	31L	-11
8	33L	23
-8	46	52
9	114	116
-9	111	-115
10	30L	-9
-10	32L	17
11	85	-69
-11	30L	3
12	51	44
-12	29	-32
3,7,L		
0	74	-83
1	119	-118
-1	26L	-5
2	28	27
-2	54	50
3	147	-164
-3	34	-33
4	289	-301
-4	254	-234
5	170	-185
-5	82	78
6	75	70
-6	31L	-27
7	33L	5
-7	32L	25
8	32L	-12
-8	84	82
9	59	60
-9	32L	3
10	41	-41
-10	31L	32
11	21L	20
-11	28L	-29
-12	24L	-0
4,7,L		
0	55	-50
1	63	-68
-1	89	-81
2	31L	7
-2	30	-25
3	82	87
-3	124	115
4	90	91
-4	39	45
5	115	-99
-5	161	-145
6	32L	20
-6	192	213
7	57	-56
-7	74	-79
8	65	60
-8	147	-148
9	45	-38
-9	107	-109
10	23	-32
-10	57	-49
-11	58	52
-12	41	50
5,7,L		
0	46	52
1	33L	-25
-1	33L	-4
2	53	57
-2	33L	-16
3	33L	15
-3	33L	-13
4	32L	-28
-4	33L	-1
5	79	-85
-5	75	77
6	29L	23
-6	32L	33
7	27L	0
-7	32L	-19
8	23L	23
-8	30L	28
9	17L	23
-9	36	45
-10	25L	-19
6,7,L		
0	101	-109
1	55	57
-1	32L	35
2	31L	1
-2	51	61
3	30L	4
-3	65	67
4	28L	-25
-4	31L	-29
5	26L	-2
-5	50	-50
6	23L	-25
-6	37	-43
7	26	35
-7	44	-38
-8	41	39
-9	36	36
7,7,L		
0	27L	11
1	58	55
-1	27L	-8
2	24L	23
-2	27L	-21
3	22L	23
-3	27L	13
4	72	-67
-4	37	31
5	28	27
-5	56	40
-6	24L	-7
-7	21L	-17
-8	18L	14
8,7,L		
0	32	-38
-1	16L	-6
-2	42	43
-3	16L	-16
-4	14L	14
0,8,L		
2	28	-32
3	86	92
4	51	41
5	42	43
6	130	120
7	39	-35
8	89	97
9	152	-142
10	20L	-12
11	18L	-5
12	38	-34
1,8,L		
0	249	-241
1	84	-75
-1	237	-208
2	19	26
-2	159	149
3	98	-94
-3	139	-144
4	17L	0
-4	17L	-2
5	40	49
-5	34	-38
6	53	59
-6	20L	22
7	65	63
-7	30	-29
8	22	19
-8	134	-136
9	21	-16
-9	21L	-13
10	19L	-3
-10	46	-2
11	73	76
-11	18L	40
12	13L	1
-12	19	19
2,8,L		
0	31	-32
1	127	-123
-1	280	267
2	48	-50
-2	168	-152
3	123	-126
-3	179	-155
4	50	-52
-4	18L	10
5	21L	-6
-5	60	-64
6	170	-161
-6	20L	-10
7	56	57
-7	34	-31
8	21L	-16
-8	22L	-8
9	52	-42
-9	48	-49
10	53	53
-10	20L	-6
11	29	-28
-11	41	-47
-12	15L	3
3,8,L		
0	72	-65
1	178	-169
-1	18L	21
2	45	-50
-2	246	212
3	37	39
-3	215	-216
4	26	-37
-4	41	43
5	140	153
-5	95	92
6	84	94
-6	30	-33
7	21L	-5
-7	118	122
8	20L	-20
-8	35	37
9	18L	-10
-9	26	34
10	39	-39
-10	19L	-14
11	10L	-9
-11	17L	28
-12	13L	7
4,8,L		
0	63	64
1	150	144
-1	52	-52
2	49	49
-2	65	69
3	50	-55
-3	115	113
4	22L	-7
-4	21L	-4
5	93	-95
-5	60	62
6	53	52
-6	22L	3
7	22	-28
-7	109	105
8	17L	17
-8	21L	8
9	14L	11
-9	19L	-13
-10	35	-42
-11	15L	-60
5,8,L		
0	22	17
1	89	-96
-1	50	55
2	35	33
-2	31	-28
3	39	46
-3	50	-48
4	65	-63
-4	35	-39
5	70	-73
-5	21	-23
6	18L	-17
-6	48	-47
7	95	82
-7	20L	-0
8	22	27
-8	19L	17
-9	52	-50
-10	14L	-10
6,8,L		
0	20L	-17
1	25	33
-1	46	-37
2	19L	12
-2	20L	-12
3	18L	13
-3	62	65
4	17L	2
-4	34	28
5	15L	14
-5	49	41
6	43	-40
-6	18L	2
-7	17L	-12
-8	15L	-11
-9	15	-23
7,8,L		
0	24	25
1	15L	-10
-1	28	27
2	13L	-4
-2	16L	-3
3	43	42
-3	16L	-8
-4	39	38
-5	54	50
-6	73	-79
0,9,L		
2	50	-55
3	41	42
4	88	88
5	58	-52
6	213	226
7	32	1
8	20L	-17
9	35	-41
10	25	-33
11	23	-28
1,9,L		
0	96	-93
1	35	-20
-1	11L	-12
2	62	56
-2	61	-54
3	67	-67
-3	53	46
4	20	25
-4	21	17
5	43	47
-5	46	-42
6	25	26
-6	77	87
7	20L	-7
-7	69	-81
8	36	-39
-8	67	75
9	27	29
-9	19L	2
10	17L	2
-10	25	-29
11	13L	-6
-11	15L	3
2,9,L		
0	212	194
1	64	-55
-1	150	-130
2	17L	-6
-2	243	-238
3	18L	21
-3	290	255
4	19L	-7
-4	90	82
5	51	-50
-5	35	-42
6	20L	-7
-6	68	68
7	20L	2
-7	90	92
8	19L	-30
-8	72	70
9	45	-49
-9	19L	-3
10	15L	-17
-10	24	33
-11	26	33
3,9,L		
0	109	-102
1	19L	8
-1	200	186
2	19L	-7
-2	42	40
3	124	120
-3	80	-74
4	20L	8
-4	19L	-11
5	64	75
-5	41	-37
6	70	75
-6	20L	-3
7	19L	0
-7	20L	-9
8	17L	3
-8	36	-41
9	20	-27
-9	21	27
10	10L	18
-10	29	30
-11	13L	-11
4,9,L		
0	46	47
1	20L	-10
-1	20L	5
2	187	-185
-2	80	-76
3	144	-153
-3	113	119
4	63	69
-4	20L	18
5	31	42
-5	46	-47
6	18L	3
-6	25	32
7	33	34
-7	19L	-3
8	31	43
-8	58	-61
-9	20	23
-10	14L	-12
5,9,L		
0	22	20
1	104	100
-1	20L	-14
2	19L	4
-2	28	28
3	19L	-5
-3	62	-66
4	18L	-4
-4	22	-28
5	16L	-2
-5	19	-18
6	14L	1
-6	90	78
7	20	-23
-7	17L	10
-8	16L	22
-9	34	-38
6,9,L		
0	17L	-14
1	17L	18
-1	24	-14
2	16L	2
-2	40	38
3	26	-30
-3	27	25
4	13L	-8
-4	17L	-11
5	20	22
-5	51	-47
-6	34	34
-7	46	50
7,9,L		
0	19	-20
1	15	-20
-1	12L	-10
-2	12L	-5
-3	32	-31
-4	30	38

than O(31) or O(32) (Fig. 1). These distances are N(3) ··· O(41), 2.61 Å; O(32)···O(41), 2·78 Å; N(3) ··· O(22), 2·62 Å; and O(31)···O(22), 2·87 Å. The angles defined by O–N–O are found to be approximately 124° with the exception of the angle defined by O(31)–N(3)–O(32), which is 128°. This larger angle is possible because the nitro group is rotated so that its oxygen atoms are not close to neighboring atoms.

Table 4. *Distance of atoms in Fig.* 1 *from plane of the six carbon atoms*

C(1)	−0·04 Å	O(61)	0·08 Å
C(2)	0·02	O(62)	0·01
C(3)	0·01	H(5)	−0·01
C(4)	−0·03	H(11)	−0·18
C(5)	0·01	H(12)	−0·20
C(6)	0·02	N(4′)	−0·72
N(1)	−0·10	O(41′)	−1·64
N(2)	0·18	O(42′)	0·46
N(3)	0·08	N(6″)	2·18
N(4)	−0·22	O(61″)	1·08
N(6)	0·03	O(62″)	2·41
O(21)	−0·50	N(1‴)	−1·63
O(22)	0·99	H(11‴)	−2·27
O(31)	−0·88	H(12‴)	−0·73
O(32)	1·08	N(1$^{\mathrm{iv}}$)	−0·92
O(41)	−0·01	H(11$^{\mathrm{iv}}$)	−0·28
O(42)	−0·10	H(12$^{\mathrm{iv}}$)	−1·83

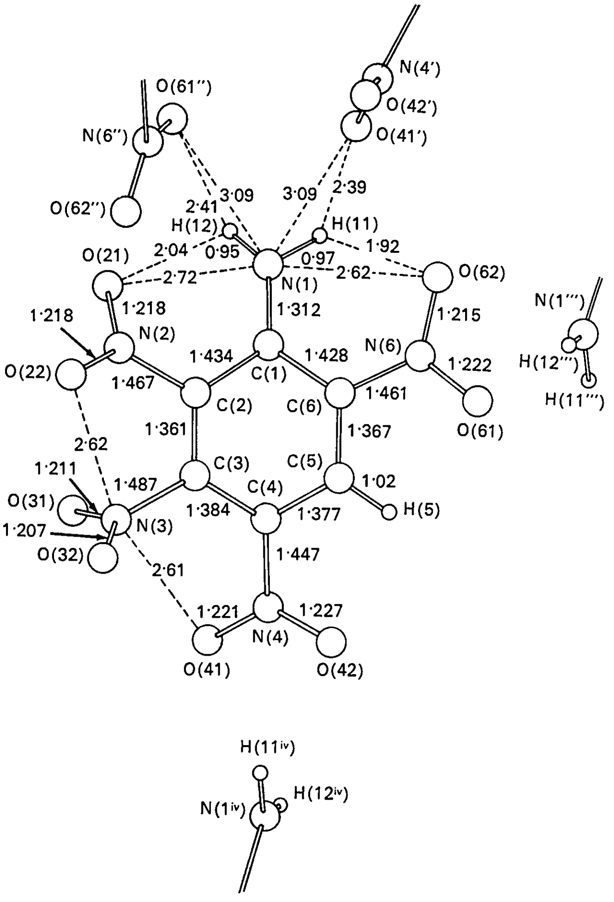

Fig. 1. Bond lengths in tetranitroaniline.

The non-bonded distances of interest at the amine group are O(61)···N(1), 2·62 Å and O(21)···N(1), 2·72 Å. Neither of these distances appear to be unusually short when compared with other non-bonded N···O distances in the molecule. It should also be noted that in 1,3,5-triamino-2,4,6-trinitrobenzene and 1,3-diamino-2,4,6-trinitrobenzene the N···O distances considered to indicate intramolecular hydrogen-bonding are more nearly 2·50 than 2·60 Å. These observations indicate that if there is intramolecular hydrogen bonding in TENA, it is of moderate strength. However, even a weak hydrogen bond of the amino group to the nitro group at C(6) might tend to keep that nitro group in a more coplanar configuration with the ring.

Intermolecular distances less than the sum of the van der Waals radii given by Pauling (1960) include H(11) to O(42′) of the molecule at $(1+x,\frac{1}{2}-y,\frac{1}{2}+z)$, 2·49 Å; O(21) to C(5$^{\mathrm{vi}}$) of the molecule at $(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$, 3·06 Å; and O(21) to H(5$^{\mathrm{vii}}$) of the molecule at $(x,\frac{1}{2}-y,\frac{1}{2}+z)$, 2·54 Å. Oxygen atom O(32$^{\mathrm{viii}}$) of the molecule at $(1-x,\ 1-y,\ -z)$ is approximately centered over the ring. The largest separation between this atom and a carbon atom of the ring is C(1)···O(32$^{\mathrm{viii}}$), 3·33 Å, while the shortest distance is C(3)···O(32$^{\mathrm{viii}}$), 3·14 Å.

The distances between N(1) and O(41′) of the molecule at $(1+x,\frac{1}{2}-y,\frac{1}{2}+z)$ and O(61″) of the molecule at $(2-x,\frac{1}{2}+y,\frac{1}{2}-z)$ are 3·09 Å in each case. The corresponding H···O distances are 2·36 and 2·42 Å. This bonding corresponds very closely to that in *p*-nitroaniline where the amino group is hydrogen bonded to nitro groups of two different molecules. In *p*-nitroaniline the N···O distances are 3·07 and 3·14 Å. These two intermolecular hydrogen-bonding networks differ in that in *p*-nitroaniline both oxygen atoms of the nitro group are involved in intermolecular hydrogen bonds to the amine groups of separate molecules, whereas in TENA the nitro groups at C(4) and C(6) have only one oxygen atom each involved in an intermolecular hydrogen bond to the amino groups of different molecules.

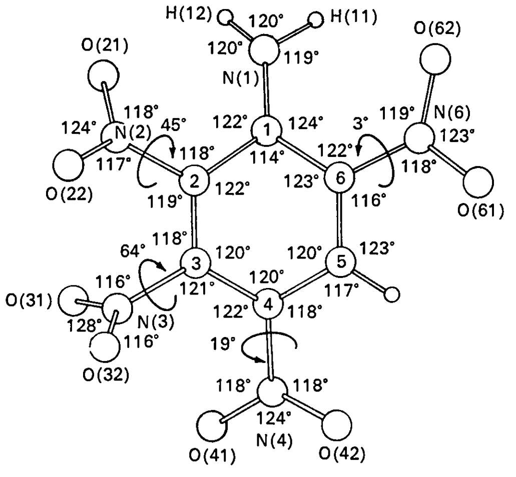

Fig. 2. Bond angles in tetranitroaniline.

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The Crystal Structures of UC_2*

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A high-temperature neutron diffraction study of UC_2 shows a tetragonal phase at 1700°C with the $C11a$ calcium carbide type structure, $a_0=3{\cdot}633$, $c_0=6{\cdot}036$ Å, $z=0{\cdot}395$, and a cubic phase at 1900°C with the $B1$ sodium chloride type structure, $a_0=5{\cdot}488$ Å. The cubic phase contains C_2 groups whose alignment was reduced to two possible cases, free rotation or random orientation along [111].

The phase diagram of the uranium–carbon system (Storms, 1965) lists a compound, uranium dicarbide, of approximate composition UC_2 existing in two high-temperature forms but unstable at room temperature. A structure has been described from room temperature studies of quenched samples (Litz, Garrett & Croxton, 1948; Austin, 1959) as tetragonal, space group $I4/mmm$, with uranium atoms in (0,0,0), carbon atoms in $(0,0,z)$, $z=0{\cdot}388$. The structure of the high temperature form has been reported from high temperature X-ray data to be the CaF_2 type (Wilson, 1960) or the FeS_2 type (Bredig, 1960).

A sample of uranium dicarbide containing excess carbon was prepared from the high-purity elements by arc-melting and pulverizing, and was examined by high-temperature neutron-diffraction (Bowman, Witteman, Arnold, Hull & Bowman, 1966). The diffraction data were obtained from $2\theta=25$ to 70° at a wavelength of 1·3926 Å, and were corrected by subtracting a blank run on the graphite sample holder. The tetragonal form was observed at 1700° and the cubic form at 1900°C. The corrected patterns are shown in Fig. 1. Observed intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to trial structures by least-squares solutions of the equation (Bacon, 1962)

$$I=K\frac{\exp(-\mu t\sec\theta)}{\sin^2 2\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2\,. \qquad (1)$$

Chemical analysis of the sample showed U 90·2%, C 9·40%, free C 0·96%, O 0·15%, N 60 ppm. Accordingly, a composition of $UC_{1.85}$ was used for the intensity calculations, with scattering factors of $0{\cdot}85\times10^{-12}$ cm for uranium and $0{\cdot}661\times10^{-12}$ cm for carbon.

The tetragonal structure previously reported was confirmed, with $K=0{\cdot}089\pm0{\cdot}007$, $B=2{\cdot}7\pm0{\cdot}6$, $z=0{\cdot}395\pm0{\cdot}003$, $R=0{\cdot}07$, where $R=\Sigma\, w|I_o-I_c|/\Sigma\, wI_o$. Lattice parameters at 1700° were $a_0=3{\cdot}633$, $c_0=6{\cdot}036$ Å, giving a C–C distance of $1{\cdot}27\pm0{\cdot}04$ Å.

The high-temperature pattern was indexed as cubic, $a_0=5{\cdot}488$ Å at 1900°, in agreement with the earlier X-ray data (Wilson, 1960). The data require a sodium

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