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The Crystal Structure of *N*-Methyl-*N*,2,4,6-tetranitroaniline (Tetryl)*

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The crystal structure of *N*-methyl-*N*,2,4,6-tetranitroaniline, or tetryl, $C_7H_5N_5O_8$, has been determined and refined by analysis of three-dimensional diffraction data from molybdenum X-radiation. The unit cell is monoclinic ($a=14\cdot129$, $b=7\cdot374$, $c=10\cdot614$ Å, $\beta=95\cdot07°$), space group $P2_1/c$, with four molecules per cell. Least-squares refinement of all positional and thermal parameters (hydrogen atoms isotropic), with 1808 reflections of non-zero weight, yielded a final weighted R index of 0·030 ($R=0\cdot06$). The final difference Fourier map indicates that conventional spherical atomic scattering factors are inadequate to describe the true electronic configuration of this molecule. None of the substituent groups is coplanar with the benzene ring. The nonplanarity of the 4-nitro group may be caused, in part, by the formation of an intermolecular hydrogen bond between the hydrogen atom attached to a benzene ring carbon and one of the oxygen atoms of the nitramine group.

Introduction

As part of an effort to understand the fundamental properties of explosives, it has been desirable to determine the crystal structures of several materials. Tetryl, one of those materials, has had a long history of military application. From a crystallographic point of view, tetryl was known to be potentially ideal for the study of the symbolic addition procedure because it is composed of equal atoms and its structure possesses a center of symmetry.

It was also of interest to see if the problem of inadequate atomic scattering factors, which was first encountered by the author in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (Cady & Larson, 1965), would be noticeable in this centrosymmetric structure. The noncentrosymmetric structure of benzotrifuroxane (Cady, Larson & Cromer, 1966), with data of the same quality as those for TATB, had failed to show evidence of residual electron density in bonding regions in the final difference Fourier maps. Maslen (1967) has shown that benzotrifuroxane is a disordered structure with about two per cent of the molecules in the disordered position. This disorder probably accounts for the fact that bonding electrons were not observed.

Experimental

Well-formed needles of tetryl with principal faces {011}, with a plane of perfect cleavage perpendicular to **a*** and elongated along **a**, were grown from a chloroform solution. A crystal cleaved from one of these needles was used for the determination of unit-cell parameters and the collection of the diffraction data. The dimensions of this crystal are 0·19 mm along **a**, 0·19 mm along **b**, and 0·29 mm along **c**. Precession photographs were used to determine preliminary unit-cell dimensions and space group extinctions ($h0l$ with l odd, and $0k0$ with k odd), and to inspect the diffraction pattern for satellites. The crystal was then transferred to a carefully aligned General Electric Company single-crystal orienter (SCO) equipped with a scintillation counter, pulse height analyzer, and molybdenum X-ray tube.

Final cell parameters and their estimated standard deviations were determined from a least-squares fit of 62 2θ (λ Mo $K\alpha_1=0\cdot70926$ Å) values greater than 20°, for hkl reflections which were measured on the SCO at 21°C. This least-squares fit gives $a=14\cdot1290\pm0\cdot0019$, $b=7\cdot3745\pm0\cdot0013$, $c=10\cdot6140\pm0\cdot0020$ Å, and $\beta=95\cdot071\pm0\cdot017°$ for the monoclinic unit cell. There are four molecules in the unit cell, and the calculated density of 1·731 g.cm^{-3} compares reasonably with a density of 1·74 g.cm^{-3} as measured by flotation.

The general technique used for obtaining accurate 2θ values may be of interest. Initial settings for the SCO are calculated from the preliminary unit-cell parameters, the lattice row which coincides with the φ axis of the SCO, and another lattice row which determines the origin of the φ circle. The diffractometer is set to a 1° take-off angle for all alignments and measurements. At $\chi=90°$ the crystal arcs are adjusted to position the lattice row which coincides with the φ axis. A small change from the initial setting of 2θ will normally be required to center a diffraction spot with respect to the left-right beam splitting device for all values of φ. Except at $\chi=90°$ the setting of φ is critical. The value of φ for a lattice row is determined by centering a low order reflection with respect to the left-right device. Small adjustments of the 2θ and φ angles are normally required in this centering. This centered lattice row is then scanned in 2θ for higher order reflections. The narrowest receiving slit which gives measurable peaks is used to obtain resolution and the peak maximum is taken to be the 2θ value for the reflection. This technique gives cell parameters which agree with those obtained from back reflection powder photographs within the calculated estimated standard deviations.

The crystal was mounted with its **a*** axis coincident with the φ axis of the SCO. Reflections within a sphere

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limited by $2\theta = 50°$ were examined by the stationary-counter, stationary-crystal technique. The intensities and background corrections were measured with balanced filters, one filter consisting of zirconium foil and the other consisting of ytterbium foil plus a small amount of aluminum foil. In addition, a background dependent on 2θ was also subtracted. This background, also measured with balanced filters, arises because of the small amount of $K\alpha$ radiation scattered by air, the glass fiber, the glue used to mount the crystal and also, perhaps, from slight unbalance of the filter pair. Within the hemisphere counted, 3865 reflections were examined. The choice of $P2_1/c$ as the space group was confirmed from examination of the space-group-extinct reflections. Of the 1936 unique space-group-allowed reflections in this set, 1808 had observed relative $F^2 > 0{\cdot}0$, and were considered observed.

Computational details

Lorentz and polarization corrections were applied. The geometry of the fragment as measured with the aid of a microscope was used in the calculation of absorption corrections (absorption coefficient = 1·726 cm^{-1}). Equivalent observed relative F^2 values were averaged, and the observed relative $|F|$ was taken as the square root of this average. The average agreement of equivalent observed reflections was estimated by forming the index $\Sigma\,|F^2 - \overline{F^2}|/\Sigma\,\overline{F^2}$ where the summation was taken over all reflections which were observed twice. This index was 0·020. A similar quantity, $\Sigma\,||F| - (\overline{F^2})^{\frac{1}{2}}|/\Sigma(\overline{F^2})^{\frac{1}{2}}$ based on $|F|$, was 0·018. This implies an ideal R of about 0·013 for the final structure if the assumptions of no systematic errors in the data and a perfect least-squares model are made.

All least-squares calculations were made with a program which uses the full matrix. The least-squares parameters included, in addition to atomic position and thermal parameters, one scale factor and one parameter to allow for secondary extinction. The secondary extinction parameter was found to be negligible and was set equal to zero in the later stages of the refinement. The quantity minimized was $\Sigma w(|F_o| - |F_c^*|)^2$, where

$$|F_c^*| = \frac{|F_c|}{K\left\{1 + g\left[\frac{2\,(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]\mathrm{Lp}|F_c|^2\right\}^{\frac{1}{2}}}$$

in which K is the scale factor, g is the extinction parameter (Zachariasen, 1963), Lp is the Lorentz and polarization factor, F_c is the calculated structure factor, and w is the weight based on counting statistics as described by Evans (1961). The weights of 'unobserved' reflections were set to 0·0. Anisotropic thermal parameters were in the form

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]\,.$$

The R index is defined as $\Sigma w(|F_o| - |F_c^*|)/\Sigma w|F_o|$.

The estimated standard deviations (e.s.d.'s) were calculated from

$$\sigma_j = \sqrt{a^{jj}\left[\frac{\Sigma\, w\,(|F_o| - |F_c^*|)^2}{m-n}\right]},$$

where m is the number of observed reflections, n is the number of parameters, and a^{jj} is the jj element of the inverse matrix. The atomic scattering factors used are those given in *International Tables for X-ray Crystallography* (1962). These scattering factors were chosen for their general availability and not for their accuracy. In particular, the scattering factor for hydrogen as calculated by Stewart, Davidson & Simpson (1965) would have been appreciably more realistic and would have improved the thermal parameters found for the hydrogen atoms.

All calculations were performed with updated versions of codes written by the author or by Larson, Roof & Cromer (1963–1965 plus other unpublished codes) unless otherwise indicated.

Determination and refinement of the structure

Normalized structure factor magnitudes, $|E|$, were calculated and sorted into classes using codes furnished by Stewart (1964). For space group $P2_1/c$

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2/\varepsilon \sum_{j=1}^{N} (f_{j\mathbf{h}})^2$$

where ε is 2 when $\mathbf{h}$ is $h0l$ or $0k0$, ε is 1 otherwise, $f_{j\mathbf{h}}$ is the atomic scattering factor for the jth atom, N is the number of atoms in the unit cell, and the $F_{\mathbf{h}}^2$ have been placed on an absolute scale and corrected for thermal motion by means of a least-squares fit of Wilson's plot.

The statistical averages and the distribution of the 1936 reflections are given in Table 1. The experimental

Table 1. *Statistical averages and distribution of* $|E|$

		Theoretical	
	Experimental	Centrosymmetric	Noncentrosymmetric
$\langle\lvert E\rvert\rangle$	0·746	0·798	0·866
$\langle\lvert E^2-1\rvert\rangle$	1·027	0·968	0·736
$\langle\lvert E\rvert^2\rangle$	1·000 (definition)	1·000	1·000
$\lvert E\rvert > 3$	0·006	0·003	0·0001
$\lvert E\rvert > 2$	0·054	0·050	0·018
$\lvert E\rvert > 1$	0·280	0·320	0·368

values correspond to a structure with a center of symmetry.

The symbolic addition procedure, which was used to determine the phases, has been used to determine the phases directly from the structure factor magnitudes for a large number of centrosymmetric structures. This procedure and its historical development are described in Karle & Karle (1966).

A code written by Bednowitz (1965) and extensively modified by the author was used to facilitate the propagation of signs and the application of the Σ_2 relationship ($sE_{\mathbf{h}} \sim s \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$ where s means 'sign of'). The five assignments listed in Table 2, together with the Σ_2 relationship, were used to calculate 106 phases with $|E| > 2{\cdot}0$.

Table 2. *Initial symbolic signs used in the application of the Σ_2 relationship*

h, k, l	$\|E\|$	Phase
5, 2, $\bar{3}$	2·524	+
9, 4, $\bar{2}$	2·767	+
11, 3, $\bar{3}$	3·415	+
10, 0, 4	5·515	*d*
11, 0, 4	3·775	*e*

It was decided that both *d* and *e* were probably + from the interactions among the signs. This assignment was made, and signs were determined for 260 reflections with $|E|$'s$>1{\cdot}5$. An E map (Fourier map with E rather than F values for coefficients) was calculated.

Coordinates for the 20 heavy atoms, as read from the E map, were used as input to the least-squares refinement. In the initial stages of the refinement, only the 1374 strongest reflections were used, while all reflections in which $I-\text{Bkgd}>0{\cdot}0$ were used in the later stages of the refinement. With one exception, the refinement proceeded normally through the steps: heavy atoms with isotropic B's, heavy atoms with anisotropic B's, and finally all atoms with anisotropic B's for heavy atoms and isotropic B's for hydrogens. The exception was that the least-squares program was limited to 196 parameters. For this reason the hydrogen positions and thermal factors were refined on alternate cycles until the problem had converged. In the next to the last cycle, all of the $\Delta\xi_i/\sigma(\xi_i)$ were less than 0·02 for the hydrogen B's except for B of H(1) which was attempting to go negative ($\Delta B_{\text{H}(1)}/\sigma_B=0{\cdot}3$). In the final cycle the largest $\Delta\xi_i/\sigma(\xi_i)$ was 0·06 for β_{13} of C(3). The final weighted R index is 0·030, while the R index with all 1808 reflections assumed to have unit weight is 0·063. The standard deviation of the electron density in the structure is estimated to be 0·064 e.Å^{-3} by Cruickshank's (1949) formula. The final least-squares parameters are given in Table 3, and the corresponding values of $K|F_o|$ and F_c are given in Table 4.

Observed and difference Fourier maps of the final structure were calculated in order to check that no important parameters had been overlooked. Even though these Fourier maps indicated that the structure was reasonable, they also pointed out the presence of a systematic error in the determination of the structure and the probable reason for much of the discrepancy between the R value obtained and that expected.

Table 3. *The final least-squares parameters and their estimated standard deviations for tetryl*

The standard deviations apply to the rightmost digits of the least-squares parameters. The anisotropic temperature factor is of the form:
$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right]$; and B is $4/3(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+\beta_{13}ac\cos\beta)$ for an anisotropic atom (Hamilton, 1959).

	X	Y	Z	$\beta_{11}\times10^5$	$\beta_{22}\times10^4$	$\beta_{33}\times10^5$	$\beta_{12}\times10^5$	$\beta_{13}\times10^5$	$\beta_{23}\times10^4$	B(Å^2)
C(1)	0.73680±20	0.04150±36	0.42398±26	293±18	122± 7	416±31	139±56	-10±38	9± 7	2.29
C(2)	0.81676±20	0.13717±37	0.47408±26	365±18	90± 6	546±32	-59±56	44±40	16± 7	2.44
C(3)	0.88023±20	0.06549±39	0.56716±28	303±19	120± 7	566±35	-224±57	-138±40	-6± 8	2.55
C(4)	0.86047±19	-0.09995±38	0.61617±26	275±17	122± 7	478±31	99±56	-190±37	10± 7	2.37
C(5)	0.78283±20	-0.20249±38	0.57284±28	329±19	113± 7	584±34	-6±55	-48±41	12± 7	2.58
C(6)	0.72440±19	-0.13025±38	0.47266±26	256±17	119± 7	616±33	-164±54	-52±38	-17± 8	2.48
C(7)	0.57226±26	0.16827±60	0.36937±37	330±23	338±12	860±46	661±89	-197±48	-14±13	4.66
N(1)	0.83549±21	0.32600±34	0.43441±25	658±22	125± 6	647±30	-309±62	-127±43	18± 7	3.65
N(2)	0.92349±19	-0.17349±34	0.72390±24	440±19	140± 7	690±31	196±53	-295±39	21± 7	3.27
N(3)	0.64641±17	-0.25016±35	0.41596±29	313±18	149± 6	1087±38	-130±51	-192±42	-24± 9	3.58
N(4)	0.66611±16	0.11300±31	0.33435±22	351±16	171± 6	466±27	161±49	-105±33	26± 7	2.89
N(5)	0.69290±21	0.16381±35	0.22085±25	662±23	160± 7	533±31	-14±62	-183±43	10± 7	3.76
O(1)	0.76941±17	0.41643±28	0.38845±23	782±19	121± 5	1292±33	275±51	-533±39	50± 6	5.00
O(2)	0.91602±18	0.37903±32	0.45160±27	715±19	237± 7	2255±46	-1490±61	-772±48	217± 9	7.15
O(3)	1.00444±16	-0.11611±33	0.73640±23	416±15	315± 7	1479±36	-526±56	-764±36	161± 8	5.75
O(4)	0.88984±15	-0.28141±28	0.79339±20	601±17	181± 6	892±28	-47±47	-366±33	107± 6	4.32
O(5)	0.60397±15	-0.33685±32	0.49055±23	495±16	270± 7	1471±35	-1315±52	247±39	10± 8	5.44
O(6)	0.63432±16	-0.25593±33	0.30145±23	663±18	298± 7	846±29	-839±54	-727±37	-20± 8	5.33
O(7)	0.63478±18	0.25049±34	0.15193±22	813±20	329± 7	888±29	705±60	-465±39	147± 8	5.96
O(8)	0.77321±16	0.12038±28	0.19525±19	568±16	218± 6	741±26	270±49	313±34	16± 6	4.15
H(1)	0.9298±17	0.1345±33	0.5985±23							0. ±0.61
H(2)	0.7717±19	-0.3391±37	0.6094±26							2.31±0.74
H(3)	0.5778±25	0.2959±45	0.3986±35							5.60±1.28
H(4)	0.5324±24	0.1402±48	0.3139±32							3.38±1.09
H(5)	0.5600±21	0.1168±42	0.4608±30							4.12±0.95

SCALE (1) = 6.8346± 82 X 10^{-1}

Table 4. *Observed and calculated magnitudes of the structure factors for tetryl*

The column headings are l, $10\,K|F_o|$, and $10\,F_c$.

H= 0 K= 0		
2	22	-6
4	157	152
6	197	-185
8	196	-186
10	46	66
12	0	-21
H= 0 K= 1		
1	315	-312
2	114	117
3	73	67
4	687	681
5	98	91
6	285	-272
7	28	18
8	55	51
9	60	60
10	11	-11
11	24	13
12	49	-52
H= 0 K= 2		
0	1154	-1143
1	853	-851
2	377	373
3	647	645
4	140	-135
5	119	108
6	82	-79
7	18	17
8	89	79
9	40	-27
10	27	-42
11	47	-48
12	41	40
H= 0 K= 3		
1	113	-115
2	716	699
3	192	-202
4	168	-160
5	75	76
6	81	-80
7	121	116
8	34	-16
9	59	60
10	38	35
11	37	-40
H= 0 K= 4		
0	588	-560
1	106	119
2	132	-125
3	23	25
4	220	-217
5	47	49
6	79	-64
7	46	-43
8	121	-115
9	54	48
10	14	24
11	21	28
H= 0 K= 5		
1	17	17
2	236	-237
3	89	98
4	22	15
5	19	-24
6	58	-63
7	102	101
8	27	-28
9	20	-36
10	15	24
H= 0 K= 6		
0	59	-76
1	146	141
2	27	25
3	138	-146
4	195	201
5	66	-65
6	0	-20
7	30	27
8	24	24
9	0	2
H= 0 K= 7		
1	21	11
2	70	73
3	31	-39
4	32	40
5	0	-12
6	73	73
7	122	-126
H= 0 K= 8		
0	27	37
1	57	-49
2	0	1
3	37	44
4	0	19
5	21	-32
H= 1 K= 0		
-12	37	35
-10	15	-21
-8	94	87
-6	319	-316
-4	887	896
-2	369	369
0	368	357
2	690	-658
4	94	-103
6	608	-572
8	192	-183
10	0	23
12	122	-118
H= 1 K= 1		
-12	0	34
-11	0	8
-10	140	-147
-9	97	-97
-8	24	33
-7	129	-128
-6	91	-90
-5	55	-54
-4	383	-389
-3	339	351
-2	517	-523
-1	233	-240
0	254	254
1	172	173
2	278	273
3	436	-426
4	112	-113
H= 1 K= 1		
5	79	-87
6	326	259
7	301	255
8	46	-60
9	107	-104
10	58	-63
11	51	46
12	0	-3
H= 1 K= 2		
-12	30	-42
-11	0	-2
-10	22	-33
-9	176	180
-8	69	74
-7	362	-364
-6	73	-74
-5	42	43
-4	123	-121
-3	702	-706
-2	167	169
-1	275	271
0	413	407
1	308	293
2	115	125
3	213	210
4	211	-202
5	46	-51
6	216	211
7	108	-109
8	15	18
9	109	109
10	0	-2
11	110	-114
12	67	65
H= 1 K= 3		
-11	91	88
-10	47	-35
-9	243	249
-8	191	-201
-7	32	30
-6	123	-124
-5	142	143
-4	60	-59
-3	319	-315
-2	120	109
-1	183	182
0	882	871
1	178	-180
2	218	-220
3	322	321
4	19	23
5	348	343
6	110	-110
7	153	-160
8	240	-235
9	61	53
10	196	183
11	144	-147
H= 1 K= 4		
-11	52	52
-10	14	-21
-9	98	93
-8	261	-266
-7	232	233
-6	179	178
-5	38	-40
-4	214	-213
-3	0	8
-2	10	2
-1	42	-26
0	353	-344
1	178	-162
2	26	25
3	10	-4
4	205	200
5	26	22
6	45	55
7	321	316
8	252	250
9	18	37
10	58	42
11	0	-9
H= 1 K= 5		
-10	0	-6
-9	52	-44
-8	23	21
-7	187	191
-6	137	137
-5	85	-89
-4	19	16
-3	4	-12
-2	162	156
-1	35	-38
0	101	-112
1	44	-60
2	148	152
3	66	58
4	116	-128
5	184	-194
6	179	-175
7	138	-132
8	104	101
9	14	17
10	61	-58
H= 1 K= 6		
-9	0	-6
-8	49	42
-7	44	47
-6	39	-45
-5	26	-27
-4	88	89
-3	45	30
-2	97	-99
-1	96	-92
0	14	12
1	40	33
2	0	-5
3	25	-35
4	100	-101
5	50	52
6	0	0
7	11	-3
8	143	-134
9	0	-1
H= 1 K= 7		
-7	70	-66
-6	138	-137
-5	75	-76
-4	35	35
-3	113	-118
-2	79	90
-1	37	-47
0	25	38
1	113	122
2	19	20
H= 1 K= 7		
3	63	67
4	60	-59
5	13	9
6	26	-53
7	1	-7
H= 1 K= 8		
-5	62	61
-4	45	54
-3	41	-46
-2	30	39
-1	61	-75
0	48	-48
1	86	-92
2	0	-21
3	31	40
4	14	-20
5	29	54
H= 2 K= 0		
-12	37	-53
-10	23	-2
-8	286	292
-6	104	97
-4	274	276
-2	928	-950
0	1016	-1023
2	8	31
4	316	310
6	77	-73
8	107	90
10	132	-114
12	0	8
H= 2 K= 1		
-12	13	19
-11	24	-21
-10	66	-63
-9	129	-131
-8	74	-70
-7	32	28
-6	283	-277
-5	7	0
-4	654	706
-3	912	931
-2	980	999
-1	711	729
0	70	65
1	372	-367
2	1002	1007
3	66	55
4	92	-90
5	124	-122
6	55	88
7	144	139
8	216	-206
9	109	-110
10	166	175
11	88	91
12	0	22
H= 2 K= 2		
-12	38	40
-11	27	29
-10	13	-10
-9	141	142
-8	84	-91
-7	157	-152
-6	30	-23
-5	83	92
-4	168	170
-3	238	-232
-2	71	-73
-1	584	589
0	106	-74
1	595	594
2	123	118
3	242	-240
4	35	26
5	20	15
6	35	-27
7	190	182
8	37	47
9	131	-125
10	44	-51
11	25	-4
12	32	-43
H= 2 K= 3		
-11	0	6
-10	58	-67
-9	68	68
-8	45	-39
-7	103	-102
-6	145	-146
-5	35	39
-4	257	247
-3	500	-493
-2	296	292
-1	339	-329
0	202	195
1	183	189
2	37	-37
3	244	-237
4	54	41
5	87	106
6	244	239
7	266	-272
8	9	-6
9	103	103
10	48	-46
11	78	-81
H= 2 K= 4		
-11	29	33
-10	57	44
-9	55	52
-8	48	53
-7	86	86
-6	50	44
-5	35	-40
-4	244	-248
-3	76	-58
-2	54	81
-1	149	-149
0	130	120
1	244	-242
2	58	-59
3	27	-31
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-5	9	15
-4	62	-73
-3	52	46
-2	55	53
-1	96	-94
0	99	97
1	74	61
2	61	59
3	20	-17
4	120	133
5	119	-127
6	14	12
7	0	7
H= 8 K= 6		
-7	17	26
-6	79	74
-5	20	14
-4	62	67
-3	40	41
-2	163	163
-1	97	-105
0	233	-245
1	60	-19
2	87	-97
3	40	-45
4	26	-27
5	47	45
6	24	46
H= 8 K= 7		
-5	23	4
-4	13	-10
-3	49	55
-2	6	-18
-1	76	70
0	133	133
1	19	32
2	5	10
3	23	-25
4	36	-47
H= 9 K= 0		
-10	17	-37
-8	259	-249
-6	62	63
-4	245	-233
-2	429	-413
0	297	283
2	345	-355
4	36	-41
6	266	-268
8	181	180
10	53	47
H= 9 K= 1		
-11	53	48
-10	45	-40
-9	96	94
-8	109	-108
-7	50	-48
-6	138	132
-5	38	-42
-4	12	9
-3	53	47
-2	92	-86
-1	8	8
0	140	-134
1	18	-22
2	27	-28
3	30	-24
4	20	32
5	76	73
6	79	-77
7	42	47
H= 9 K= 1		
8	98	97
9	15	24
H= 9 K= 2		
-10	28	-28
-9	15	10
-8	115	106
-7	217	217
-6	32	-30
-5	74	-83
-4	55	52
-3	59	-58
-2	15	13
-1	217	217
0	31	27
1	139	-140
2	74	85
3	81	73
4	17	2
5	102	-102
6	163	169
7	103	110
8	81	-82
9	0	22
H= 9 K= 3		
-10	12	-30
-9	47	-44
-8	110	-114
-7	17	-18
-6	42	-40
-5	30	-27
-4	35	34
-3	40	-41
-2	111	-109
-1	108	113
0	21	11
1	142	145
2	20	-7
3	13	16
4	65	-71
5	100	-112
6	97	-111
7	13	-37
8	62	-78
9	15	-21
H= 9 K= 4		
-9	100	101
-8	0	19
-7	28	-27
-6	27	20
-5	50	-46
-4	194	207
-3	322	-327
-2	302	313
-1	89	-87
0	18	-6
1	20	-27
2	87	89
3	115	119
4	20	-25
5	114	118
6	37	-47
7	62	-68
8	0	18
H= 9 K= 5		
-8	0	0
-7	79	76
-6	3	4
-5	18	-11
-4	15	23
-3	87	-88
-2	119	118
-1	123	-129
0	73	68
1	91	-88
2	28	37
3	25	29
4	47	-55
5	0	17
6	14	-1
7	15	-30
H= 9 K= 6		
-6	18	30
-5	17	17
-4	61	-65
-3	54	45
-2	64	-60
-1	130	-134
0	175	-172
1	52	54
2	59	-69
3	0	-5
4	20	18
5	20	17
H= 9 K= 7		
-4	23	31
-3	12	4
-2	82	96
-1	27	19
0	89	98
1	43	51
2	17	5
H= 10 K= 0		
-10	33	41
-8	65	63
-6	184	-180
-4	31	36
-2	154	-141
0	0	33
2	31	37
4	625	652
6	208	224
8	20	24
H= 10 K= 1		
-10	45	41
-9	27	29
-8	14	13
-7	8	0
-6	68	70
-5	61	73
-4	0	1
-3	199	192
-2	204	-186
-1	2	0
0	126	128
1	154	156
2	180	-177
3	204	-216
4	99	101
5	75	-84
6	48	53
7	63	74

Table 4 (*cont.*)

H= 10 K= 1		
8	39	36
9	14	6
H= 10 K= 2		
-10	28	-31
-9	80	81
-8	21	-5
-7	24	-21
-6	8	-6
-5	111	111
-4	17	-19
-3	107	-101
-2	10	-17
-1	14	-18
0	11	-12
1	81	-74
2	62	55
3	85	77
4	81	-84
5	124	-136
6	41	-40
7	32	26
8	0	-2
9	16	37
H= 10 K= 3		
-9	89	-86
-8	71	-74
-7	87	-95
-6	24	-13
-5	28	-36
-4	54	53
-3	56	-56
-2	144	139
-1	195	188
0	157	156
1	193	-199
2	153	-172
3	35	39
4	66	-76
5	38	-39
6	90	107
7	36	-44
8	14	-2
H= 10 K= 4		
-8	41	49
-7	16	4
-6	117	118
-5	105	-92
-4	46	-45
-3	151	-154
-2	31	-17
-1	26	-10
0	105	-98
1	108	58
2	38	-45
3	42	54
4	143	-154
5	0	3
6	0	-21
7	21	45
H= 10 K= 5		
-7	52	52
-6	26	-28
-5	5	6
-4	18	-10
-3	30	26
-2	52	55
-1	73	-70
0	57	-46
1	47	-21
2	116	123
3	49	56
4	27	-37
5	19	44
6	50	-64
H= 10 K= 6		
-5	45	-63
-4	31	-30
-3	42	37
-2	5	-1
-1	25	15
0	93	89
1	49	47
2	0	5
3	20	-31
4	0	2
H= 10 K= 7		
-1	50	-46
0	38	-38
H= 11 K= 0		
-10	44	56
-8	0	-6
-6	18	0
-4	20	-13
-3	0	0
-2	160	-162
0	147	136
2	228	223
4	360	380
6	60	-66
8	21	-20
H= 11 K= 1		
-10	13	-13
-9	42	-43
-8	39	31
-7	61	64
-6	169	-161
-5	118	-122
-4	61	63
-3	78	78
-2	31	39
-1	62	-64
0	132	-135
1	53	-54
2	218	-230
3	116	-117
4	54	51
5	54	-51
6	30	35
7	14	8
8	0	21
H= 11 K= 2		
-9	0	2
-8	3	7
-7	28	-28
-6	57	-66
-5	36	31
-4	109	106
-3	174	-175
-2	91	90
-1	83	-90
0	94	-92
1	15	1
2	63	67
3	49	-51
4	21	-19
5	27	-36
6	23	31
7	103	115
8	0	-8
H= 11 K= 3		
-9	21	22
-8	17	14
-7	2	11
-6	132	-136
-5	270	272
-4	15	10
-3	17	6
-2	109	-117
-1	126	137
0	0	-14
1	82	-80
2	69	56
3	77	79
4	17	36
5	31	41
6	72	91
7	0	13
H= 11 K= 4		
-8	0	-11
-7	0	5
-6	19	-11
-5	77	79
-4	159	-205
-3	122	117
-2	97	-95
-1	41	44
0	46	58
1	45	-48
2	127	-134
3	0	-16
4	68	-80
5	30	-38
6	15	-1
H= 11 K= 5		
-6	42	49
-5	0	2
-4	72	-69
-3	31	42
-2	172	177
-1	71	-70
0	49	56
1	62	55
2	50	54
3	40	-46
4	4	4
5	14	6
H= 11 K= 6		
-4	0	-22
-3	31	42
-2	14	14
-1	71	68
0	0	1
1	20	1
2	4	21
3	6	-31
H= 12 K= 0		
-8	42	-35
-6	126	124
-4	17	22
-2	186	191
0	96	85
2	254	-259
4	43	56
6	172	-176
H= 12 K= 1		
-9	53	-51
-8	54	50
-7	0	-2
-6	50	-49
-5	92	-93
-4	33	52
-3	51	-51
-2	40	-43
-1	11	-20
0	9	-11
1	105	106
2	239	250
3	198	208
4	117	-118
5	40	-34
6	121	129
7	51	-69
H= 12 K= 2		
-9	14	10
-8	13	8
-7	95	92
-6	33	-32
-5	36	38
-4	12	6
-3	72	79
-2	109	-112
-1	14	13
0	17	28
1	184	-187
2	17	14
3	218	234
4	23	-29
5	31	39
6	83	90
7	52	47
H= 12 K= 3		
-8	23	-29
-7	58	55
-6	107	-109
-5	114	108
-4	59	-100
-3	14	-11
-2	22	-18
-1	9	-8
0	94	99
1	57	-77
2	62	63
3	143	-149
4	81	101
5	0	11
6	0	-8
H= 12 K= 4		
-7	0	4
-6	38	-37
-5	82	78
-4	25	32
-3	63	64
-2	35	31
-1	28	-25
0	105	-110
2	71	83
3	85	-99
4	44	-32
5	0	-18
H= 12 K= 5		
-5	5	-1
-4	14	-21
-3	18	19
-2	4	5
-1	0	3
0	35	-35
1	0	4
2	5	-4
3	0	-26
4	4	2
H= 12 K= 6		
-2	6	3
-1	27	-28
0	64	65
H= 13 K= 0		
-8	33	30
-6	15	15
-4	115	108
-2	0	-2
0	23	8
2	283	-293
4	53	42
6	65	-67
H= 13 K= 1		
-8	0	4
-7	17	-14
-6	84	-84
-5	27	31
-4	94	-102
-3	0	-8
-2	19	-18
-1	116	119
0	122	122
1	225	236
2	105	97
3	42	55
4	71	69
5	13	-21
6	21	15
H= 13 K= 2		
-8	21	26
-7	38	-23
-6	35	33
-5	26	28
-4	25	-18
-3	105	-104
-2	17	-12
-1	10	-12
0	23	-9
1	167	-175
2	40	-42
3	133	142
4	28	-31
5	119	-125
6	30	31
H= 13 K= 3		
-7	46	-57
-6	84	84
-5	81	-82
-4	32	-34
-3	49	-43
-2	46	45
-1	56	-56
0	66	68
1	89	-102
2	22	-8
3	0	0
4	29	32
5	34	-42
H= 13 K= 4		
-6	39	41
-5	5	14
-4	12	7
-3	101	102
-2	16	-12
-1	12	0
0	105	-113
1	68	65
2	103	114
3	14	13
4	3	-13
H= 13 K= 5		
-4	0	-3
-3	0	-13
-2	33	-31
-1	22	-29
0	0	-2
1	51	-63
2	17	33
H= 14 K= 0		
-6	128	-127
-4	30	-26
-2	107	-113
0	145	149
2	0	-29
4	100	-122
6	45	-55
H= 14 K= 1		
-7	4	-7
-6	12	21
-5	3	25
-4	35	43
-3	62	58
-2	0	-4
-1	10	-18
0	57	63
1	42	-34
2	50	45
3	51	-51
4	26	4
5	0	3
H= 14 K= 2		
-7	129	-131
-6	54	52
-5	13	-6
-4	51	52
-3	63	-74
-2	19	-5
-1	176	177
0	91	-93
1	11	-6
2	56	-58
3	0	-8
4	30	35
5	15	-4
H= 14 K= 3		
-6	66	65
-5	42	-41
-4	5	4
-3	32	-29
-2	55	-59
-1	83	82
0	22	-7
1	54	63
2	14	4
3	34	39
4	20	26
H= 14 K= 4		
-4	48	-50
-3	5	2
-2	33	42
-1	6	-19
0	15	-3
1	44	57
2	69	70
H= 15 K= 0		
-6	17	-16
-4	70	74
-2	60	63
0	38	52
2	0	30
4	0	-1
H= 15 K= 1		
-6	24	30
-5	5	8
-4	65	72
-3	46	47
-2	109	-114
-1	72	-74
0	87	-82
1	96	-101
2	15	-20
3	34	32
4	105	-108
H= 15 K= 2		
-5	0	13
-4	40	-45
-3	79	78
-2	23	-21
-1	173	180
0	86	84
1	54	67
2	25	-26
3	62	75
H= 15 K= 3		
-4	17	21
-3	37	-49
-2	25	-27
-1	44	-44
0	0	-9
1	36	29
2	0	-5
H= 16 K= 0		
-4	23	8
-2	79	-76
0	0	-3
2	30	-33
H= 16 K= 1		
-4	6	-17
-3	40	-34
-2	13	-22
-1	33	-34
0	43	-42
1	26	-40
2	31	-41
H= 16 K= 2		
-3	17	15
-2	110	111
-1	27	34
0	43	45
1	0	-5

Fourier maps illustrating this error are given in Figs. 1, 2, and 3. This error, which is caused by neglecting bonding effects on the atomic scattering factor, has been observed by Cady & Larson (1965), Hanson (1966), and Fritchie (1966), among others, and is discussed in detail by Stewart, Davidson & Simpson (1965), Rae & Maslen (1965), O'Connell, Rae & Maslen (1966), and Dawson (1965).

Further refinement of tetryl should be profitable with nonspherical atomic scattering factors that allow for bonding effects, but this was not attempted here. The use of better atomic scattering factors would be expected to cause noticeable shifts in the positions of the hydrogen and oxygen atoms and significant shifts in the thermal parameters of all of the atoms. The largest shifts in the hydrogen and oxygen parameters should be such as to lengthen the C–H and N–O bonds and reduce the apparent thermal motion of the atoms parallel to these bonds.

Discussion of the structure

The above-mentioned shifts would invalidate any detailed analysis of bond length corrections and their relation to thermal motion at this time. On the other hand, the structure is well determined according to the present state of the art. Positions of the heavy atoms should change very little when better scattering factors are used so that a discussion of the uncorrected interatomic distances, bond angles, and molecular packing is meaningful.

Intramolecular bond distances and angles are given in Fig. 4. With the inclusion of correlation terms and e.s.d.'s for the unit-cell parameters in the calculations, the e.s.d.'s of the bond distances are less than 0·004 Å for heavy-atom bonds and 0·03 Å for those involving hydrogen atoms. The e.s.d.'s for the angles are less than 0·3° for heavy–heavy–heavy, 3° for heavy–heavy–hydrogen, and 4° for hydrogen–heavy–hydrogen bond angles. None of the nonbonded intramolecular distances is less than Bartell's (1960) hard-shell distances, so the existence of intramolecular hydrogen bonds is ruled out.

The bond distances and angles in tetryl appear to be normal when compared with results obtained with three-dimensional data in other recent structure determinations of nitrobenzene derivatives (Trotter, 1959, nitrobenzene; Coppens & Schmidt, 1964, *o*-nitrobenzaldehyde; Sax, Beurskens & Chu, 1965, *o*-nitroperoxybenzoic acid; Hamilton & La Placa, 1964, methyl ester of *o*-nitrobenzenesulfenic acid; Trotter & Williston, 1966, *m*-dinitrobenzene; Coppens & Schmidt, 1965*a*, *b*, *p*-nitrophenol; Trueblood, Goldish & Donohue, 1961, 4-nitroaniline; Mak & Trotter, 1965, *N*,*N*-dimethyl-*p*-nitroaniline; Boonstra, 1963, 4,4′-dinitrodiphenyl; McPhail & Sim, 1965, 2-chloro-4-nitroaniline; Ferguson & Sim, 1962, 2-chloro-5-nitrobenzoic acid; Brown, Wallwork & Wilson, 1964, Hanson, 1964, 1965, 1966, Williams & Wallwork, 1966, Carter, McPhail & Sim, 1966, *s*-trinitrobenzene complexes; Struchkov & Khotsyanova, 1960, 2,6-dichloro-4-nitrodimethylaniline; Bailey & Prout, 1965, picrylazide complex; Harris, 1964, picryl chloride; Palenik, Bettman & Hughes, 1966, potassium picrate; Holden & Dickinson, 1967, 1,3-dichloro-2,4,6-trinitrobenzene; Holden, 1967, 1,3-diamino-2,4,6-trinitrobenzene; Holden, Stewart & Dickinson, 1966, 2,3,4,6-tetranitroaniline; Cady & Larson, 1965, 1,3,5-triamino-2,4,6-trinitrobenzene; Akopyan, Struchkov & Dashevskii, 1966, hexanitrobenzene; Akopyan, Kitaigorodskii & Struchkov, 1965, 1,8-dinitronaphthalene). Bailey & Prout (1965) have mentioned the general occurrence of internal angles greater than 120° at the carbon atoms attached to nitro groups. Carter *et al.* (1966) propose a reasonable explanation for this effect which would explain why the size of this internal angle is independent of the rotation angle of the nitro group with respect to the benzene ring. Angles larger than 120° for the O–N–O angle have been recognized for some time. The structures in which the O–N–O angle is less than 120° have either steric problems associated with two *ortho* substituents which have intramolecular forces strong enough to hold the nitro group in the plane of the benzene ring, or two adjacent negatively charged groups. Examples are 1,3,5-triamino-2,4,6-trinitrobenzene and the nitranilate ion (Jensen & Andersen, 1964). Bond lengths in nitrobenzene derivatives which have exceptionally numerous and stable resonance forms [1,3,(5)-di(tri)-amino-2,4,6-trinitrobenzene or the nitranilate ion] are significantly different from those in tetryl.

The direction cosines and distances from the origin of the least-squares planes through several groups of atoms in tetryl are given in Table 5, together with the angles between these planes and the benzene ring. As can be seen from the deviations of the atoms from these planes (Table 6) it is unlikely that most of these groups are truly planar; however, there can be no question that the methylnitramine and nitro groups are bent and twisted with respect to the aromatic nucleus. The C(1)–N(4), C(2)–N(1), C(4)–N(2), and C(6)–N(3) bonds are bent +5, +4, +3, and −5°, respectively, from the plane of the ring. These bends make an insignificant contribution to the rotation angles between the normals of the planes given in Table 5. In addition, it is apparent from Fig. 5 that the nitro groups adjacent to the methylnitramine group have rotated slightly in the plane of the benzene ring [angles C(1)–C(2)–N(1) and C(1)–C(6)–N(3)] so as partially to relieve the overcrowding near C(1). This type of rotation has been observed in all of the aromatic compounds mentioned in this paper in which there are *ortho* substituents. Dashevskii, Struchkov & Akopyan (1966) have discussed in detail packing effects and the expected bond deformations and nitro group rotations in nitrobenzene derivatives.

The only substituent groups on an aromatic ring which have been studied and which do not repel *ortho* nitro groups sufficiently to twist them from the plane of the benzene ring are the relatively small hydrogen atom and the hydrogen-bonding amine group. Since the nitro group attached to C(4) has only hydrogen atoms *ortho* to it, it would be expected to be nearly coplanar with the benzene ring; however, it is rotated from this plane by about 24°. This rotation must be caused by some intermolecular force, possibly the hydrogen bond which is discussed in the following paragraphs.

The hydrogen atoms are poorly located by the least-squares refinement as is evidenced by the large spread in C–H bond distance, and it was felt that the interatomic distances involving hydrogen atoms could be better obtained from a model than from the refinement. An admittedly arbitrary model was constructed by adjusting only the C–H bond lengths for H(1), H(2), and H(4) to 1·085 Å, while adjusting both the bond lengths and angles involving H(3) and H(5) to obtain tetrahedral angles at C(7). Assuming van der Waals radii of 1·57, 1·50, 1·40, and 1·20 Å for carbon, nitro-

Fig. 1. Final difference Fourier map of the section through the aromatic ring. Contour interval 0·05 e.Å^{-3}, negative contours light lines, zero contour dotted.

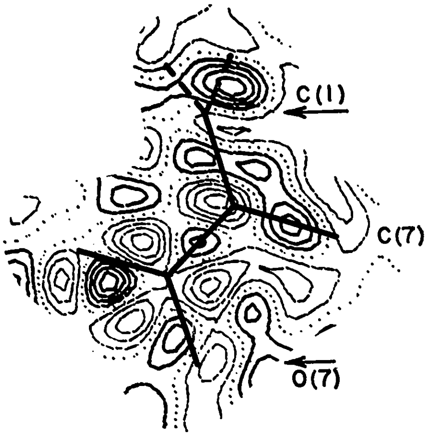


Fig. 2. Final difference Fourier map of the section through the nitramine group. Contour interval 0·05 e.Å^{-3}, negative contours light lines, zero contour dotted.

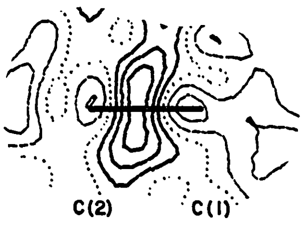


Fig. 3. Final difference Fourier map of the section through the C(1)–C(2) bond and perpendicular to the plane of the aromatic ring. Contour interval 0·05 e.Å^{-3}, negative contours light lines, zero contour dotted.

Table 5. *Least-squares planes**

Direction cosines with respect to **a**	**b**	**c***	Distances from origin	Description of plane	Angle with aromatic ring
−0·6039	0·4187	0·6782	2·893 Å	(1) Aromatic ring	—
−0·2571	0·3265	0·9096	−2·036	(2) C(2), N(1), O(1), O(2)	25°
−0·3351	0·7449	0·5769	0·673	(3) C(4), N(2), O(3), O(4)	23†
−0·6613	0·7497	0·0233	7·076	(4) C(6), N(3), O(5), O(6)	44
0·3414	0·8534	0·3939	−5·148	(5) N(4), N(5), O(7), O(8), C(7)	65

* For the molecule whose coordinates are given in Table 3.
† Rotation is in the opposite sense from the other planes.

Table 6. *Deviation of atoms* (Å) *from least-squares planes**

	Plane (1)	(2)	(3)	(4)	(5)
C(1)	**0·015**				0·219
C(2)	**0·015**	**0·001**			
C(3)	**−0·027**				
C(4)	**0·010**		**0·002**		
C(5)	**0·020**				
C(6)	**−0·033**			**−0·004**	
C(7)	1·388				**0·013**
N(1)	0·132	**−0·003**			
N(2)	0·078		**−0·009**		
N(3)	−0·177			**0·013**	
N(4)	0·145				**−0·017**
N(5)	−0·805				**−0·004**
O(1)	0·619	**0·001**			
O(2)	−0·259	**0·001**			
O(3)	−0·338		**0·003**		
O(4)	0·570		**0·003**		
O(5)	0·495			**−0·005**	
O(6)	−0·977			**−0·005**	
O(7)	−0·574				**−0·004**
O(8)	−1·822				**0·011**
H(1)	0·005				
H(2)	−0·024				
H(3)	1·961				
H(4)	1·212				
H(5)	2·040				

* Bold face type indicates that the atom was used to define the plane.

gen, oxygen, and hydrogen, respectively, the list of all intermolecular interatomic distances was examined for distances shorter than those that would be predicted from the van der Waals radii. Only four such intermolecular distances, H(1)–O(3′) (2·50 Å), H(4)–O(6′) (2·46 Å), H(5)–O(7′) (2·49 Å), and H(2)–O(8′) (2·28 Å), were found. The last two of these are longer in the model than in the determined structure. The pertinent angles and distances are given in Table 7.

The 'bond' from H(2) to O(8′) appears to be a weak, but conventional hydrogen bond in that the O–H distance is 0·3 Å less than the van der Waals contact distance, the H(2)–O(8′)–N(5′) angle approximates a normal bond angle for an oxygen vertex atom, and the C(5)–H(2)–O(8′) angle is nearly 180°. Additional crystallographic information which supports the formation of this hydrogen bond is found by examination of the thermal motions of N(4), N(5), O(7), and O(8), and their associated rigid body oscillations. The major os-

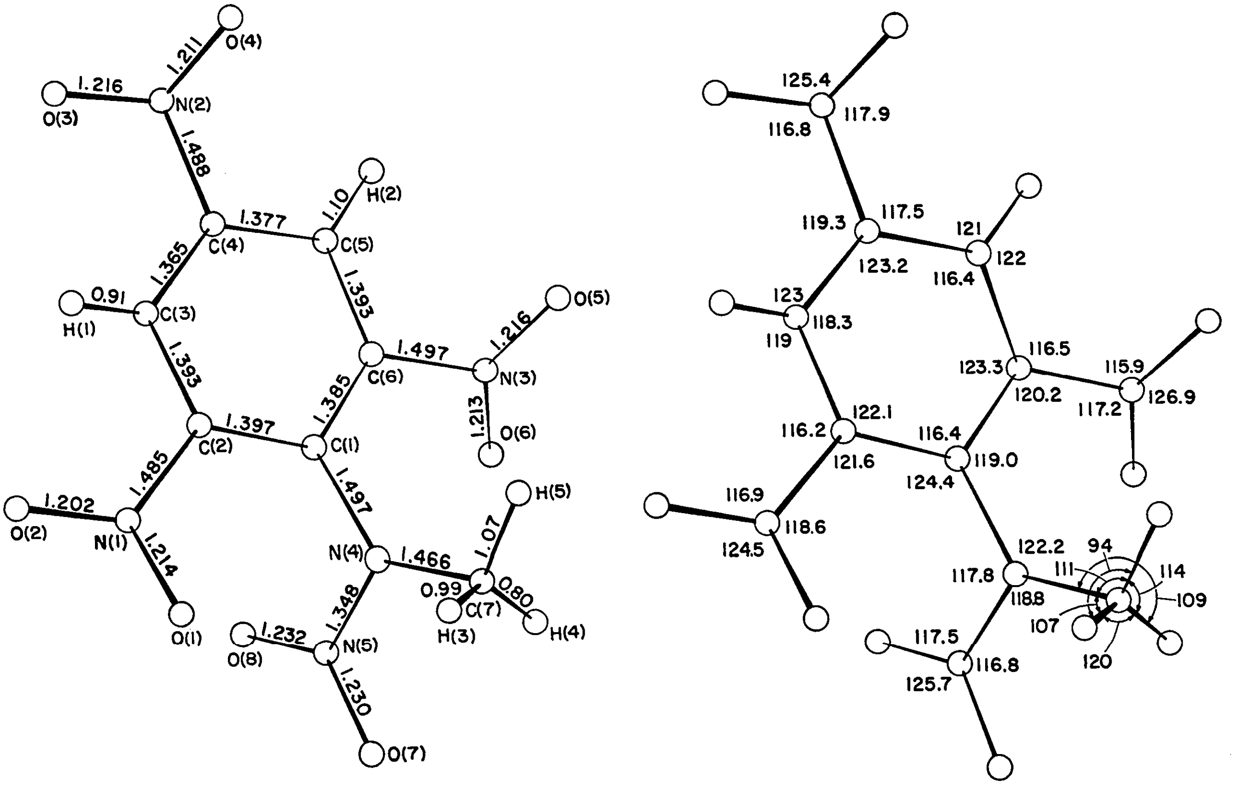
Table 7. *Distances and angles in intermolecular 'hydrogen bonds'*

Type	Distance	Type	Angle
C(3)–O(3′)	3·39 Å	C(3)–O(3′)–N(2′)	106°
H(1)–O(3′)	2·50	H(1)–O(3′)–N(2′)	94
		H(1)–C(3)–O(3′)	29
		C(3)–H(1)–O(3′)	131
C(7)–O(6′)	3·34	C(7)–O(6′)–N(3′)	126
H(4)–O(6′)	2·46	H(4)–O(6′)–N(3′)	118
		H(4)–C(7)–O(6′)	29
		C(7)–H(4)–O(6′)	138
C(7)–O(7′)	3·11	C(7)–O(7′)–N(5′)	142
H(5)–O(7′)	2·49	H(5)–O(7′)–N(5′)	159
		H(5)–C(7)–O(7′)	47
		C(7)–H(5)–O(7′)	114
C(5)–O(8′)	3·35	C(5)–O(8′)–N(5′)	113
H(2)–O(8′)	2·28	H(2)–O(8′)–N(5′)	111
		H(2)–C(5)–O(8′)	6
		C(5)–H(2)–O(8′)	171

cillation axis of the group is not defined by the N(4)–N(5) vector, as would be expected in a free nitro group, but is more nearly the N(4)–O(8) vector and indicates a restriction on the motion of O(8) as would be expected if it is involved in a bond which is nearly perpendicular to the plane of the nitro group. It can also be postulated that the apparent long C(5)–H(2) bond of 1·10 Å is caused by a shift in the position of the electron cloud near H(2) relative to the position in a normal covalent bond.

A similar calculation of the intermolecular interatomic distances and angles in potassium picrate (Palenik *et al.*, 1966) and 2,3,4,6-tetranitroaniline (Holden *et al.*, 1966) indicates the presence of the same type of C–H---O bond.

The remaining three weaker 'hydrogen bonds' in tetryl are indicative of an ionic attraction between a partially shielded proton (electrons concentrated in C–H bond) and negatively charged oxygen atoms of the nitro groups. Close intermolecular approaches of hydrogen atoms and oxygen atoms of nitro groups have been calculated in nearly all nitro compounds the author has investigated. Many of these close approaches would not seem to be hydrogen bonds in the



(*a*) (*b*)

Fig. 4. (*a*) Bond distances (Å), (*b*) bond angles (°) in tetryl.

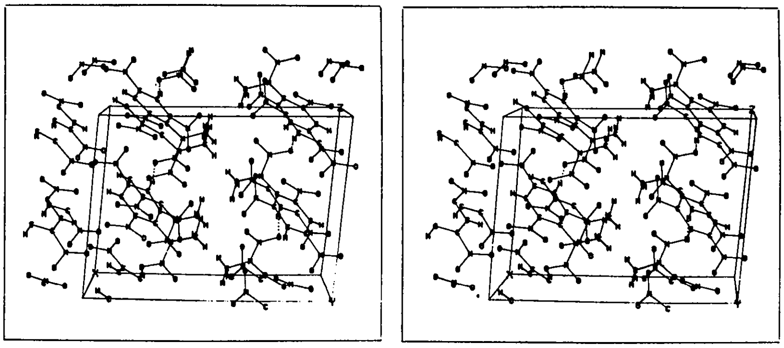


Fig. 5. Stereo pair illustrating the molecular packing in tetryl.

conventional sense, principally because of the large deviations of the hydrogen atoms from the C---O, or in the case of amines N---O, vectors. The stronger H(2)–O(8′) interaction in tetryl can also be interpreted as an especially favorable case of this electrostatic attraction.

The molecular packing in the unit cell is illustrated by the stereo pair in Fig. 5. The direction of view is 7° from **b** toward **c*** and 3° toward −**a**. The monoclinic unit cell is outlined. Covalently bonded atoms are connected by solid lines, and the O(8′)–H(2) bond is represented by a dotted line. All atoms which are within the volume bounded by $-0{\cdot}005 \le x \le 1{\cdot}250$, $0{\cdot}0 \le y \le 1{\cdot}5$, and $0{\cdot}0 \le z \le 1{\cdot}350$, and which are bonded to at least one other atom in this volume are included.

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