Table 3. *Equation of least-squares plane through* N(1), N(2), O(1) *and* O(3) *and deviations* (Å) *of atoms from the plane*

Equation: $0{\cdot}8802X - 0{\cdot}4016Y + 0{\cdot}2528Z = -1{\cdot}4348$.

Cu	−0·201 (1)	C(2)	0·022 (4)
O(1)	0·013 (3)	C(3)	0·015 (5)
O(2)	0·099 (5)	C(4)	−0·674 (5)
O(3)	−0·013 (3)	C(5)	0·035 (5)
O(4)	0·189 (5)	C(6)	0·170 (4)
N(1)	−0·013 (3)	C(7)	0·117 (4)
N(2)	0·013 (3)	C(8)	0·055 (6)
C(1)	0·038 (4)	C(9)	0·401 (6)

of the non-H atoms are on the same side of the plane except the ring atom C(4). All of the intraligand distances are in reasonable agreement with those previously observed. There is considerable distortion in bond angles from the expected tetrahedral and trigonal values, presumably required in order to achieve the tetradentate bonding.

Both water H atoms participate in hydrogen bonding. The hydrogen bonds O(5)—H(O5)···O(2) ($-x, 1-y, 1-z$) and O(5)—H′(O5)···O(4) ($-x, 1-y, -z$) are 2·863 (5) and 2·719 (4) Å with acceptor distances of 2·03 (6) and 1·99 (5) Å and hydrogen-bond angles 166 (5) and 174 (7)°. These bonds link molecules related by a translation along the *c* axis with formation of chains in the **c** direction.

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Structure of Barium 2,4,6-Trinitroresorcinolate Monohydrate

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Abstract. $C_6HN_3O_8^{2-}.Ba^{2+}.H_2O$ (BaTNR), monoclinic, $P2/c$, $a = 7{\cdot}546\,(8)$, $b = 8{\cdot}082\,(5)$, $c = 8{\cdot}756\,(3)$ Å, $\beta = 106{\cdot}52\,(5)°$, $V = 513{\cdot}16$ Å^3, $D_c = 2{\cdot}58$ Mg m^{-3}, $Z = 2$. The structure was solved by the Patterson method and refined by the least-squares method to a final R factor of 0·051 for 963 observed reflections. The Ba atom is surrounded by nine O atoms, the Ba—O distances ranging from 2·694 (14) to 2·899 (16) Å.

Introduction. Lead, barium and silver salts of nitrophenol and polynitrophenol have good detonating properties and are sensitive to flames; therefore, they can be used as initiating agents, and as igniter powder or delay powder. Seldom, however, has their structure been reported. In order to study the structural features of BaTNR and to compare them with the structure of the related lead compound (normal salt, N-LTNR) reported earlier by Reed (1959), we have determined the crystal structure of BaTNR.

Experimental. Crystals of BaTNR appear in the forms of yellow chips and elongated prisms. They belong to point group C_{2h}. A single crystal approximately 0·3 × 0·3 × 0·1 mm was selected for the experiment. Preliminary cell parameters were obtained by means of rotation and Weissenberg photography. The possible space groups are $P2/c$ and Pc from the systematic absences ($h0l$ absent when l odd). Accurate cell parameters were obtained with a four-circle diffractometer.

Intensities of 963 observed reflections within the range $3° \leq \theta \leq 26°$ were collected on a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation employing the θ–2θ scan technique. All the reflection data were corrected for Lorentz and polarization factors, but not for absorption. The scale and temperature factors were obtained by Wilson's statistical method.

The space group $P2/c$ was assumed and this was confirmed at a later stage by intensity calculations. The calculated density indicates that there are two BaTNR molecules in a unit cell. This requires that the Ba atoms must be on a set of special positions. The Patterson synthesis showed that the Ba atom was on a twofold axis. Accordingly, Ba atoms can be located on either of

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Table 1. *The atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors*

Standard deviations are given in parentheses. The temperature factor is of the form: $T = \exp(-B \sin^2 \theta/\lambda^2)$.

	x	y	z	B_{eq} (Å^2)
C(1)	3464 (21)	1367 (19)	6394 (16)	0·99
C(2)	3617 (20)	3135 (20)	6398 (17)	1·31
C(3)	5000	4006 (26)	7500	1·05
C(4)	5000	635 (28)	7500	1·15
N(1)	2421 (18)	4139 (17)	5191 (15)	1·31
N(2)	5000	−1203 (21)	7500	0·97
O(11)	2129 (14)	517 (14)	5544 (12)	1·40
O(1)	999 (18)	3537 (14)	4250 (13)	2·12
O(2)	2746 (21)	5642 (17)	5113 (10)	2·95
O(3)	3687 (17)	−1888 (15)	7809 (14)	2·14
O(4)	0	2751 (25)	7500	3·14
Ba	0	635 (5)	2500	1·10

two sets of special positions: 2(*e*) $(0,y,\frac{1}{4};\ 0,\bar{y},\frac{3}{4})$ or 2(*f*) $(\frac{1}{2},y,\frac{1}{4};\ \frac{1}{2},\bar{y},\frac{3}{4})$ (*International Tables for X-ray Crystallography*, 1952). The position of the Ba atom was set at $(0,0{\cdot}0635,\frac{1}{4})$, where the y parameter was deduced from the Patterson maps. The structure factors calculated on the basis of the heavy-atom positions gave an R value of 0·24. All the non-hydrogen atoms were located from the difference Fourier synthesis, and the R factor reduced to 0·096. The coordinates and anisotropic thermal parameters of the non-hydrogen atoms have been refined by the least-squares method, and the R factor was further reduced to a final value of 0·051. The final atomic parameters are listed in Table 1.*

Discussion. All bond lengths and angles are given in Fig. 1. The molecule has twofold symmetry, with its axis passing through C(3), C(4) and N(2) located on the crystallographic twofold axis (see Fig. 2).

The benzene ring is slightly twisted. O(11) deviates only 0·058 Å from the least-squares plane of the ring, so can be considered to be essentially on the plane. The equation of the least-squares plane and the deviations of the atoms from it are given in Table 2.

It has been observed that the bond angles at C atoms having nitro groups as substituents are significantly larger than those at C atoms having H 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 C σ orbital to the N atom, and increasing the s character of the C σ orbital to the adjacent C atoms, thus causing the bond angles to be greater than 120°. In agreement with these observations, the nitro-substituted C atoms in BaTNR have C—C—C bond angles of 122·7 (15)° at C(2) and 130·6 (8)° at C(4). The H-substituted ring atom has a C—C—C bond angle of 119·8 (8)°. The p electron on O^- of the ring is conjugated with a π bond on the benzene ring, causing the C(1)—O(11) bond length to be shortened and the C—C(1)—C bond angle to be less than 120°. Similar bond angles were observed in N-LTNR and potassium picrate (Maartmann-Moe, 1969).

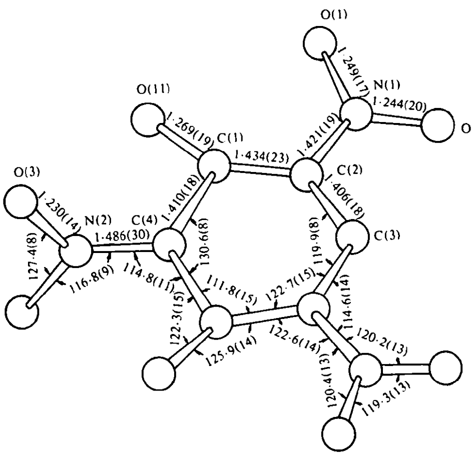

Fig. 1. The molecular configuration and atom-naming scheme with bond distances (Å) and angles (°).

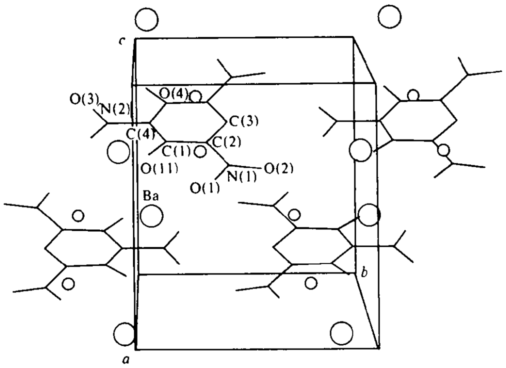

Fig. 2. A perspective drawing showing the packing of the two molecules in the unit cell, and the portions of adjacent molecules in neighboring cells. Large circles represent Ba atoms and small ones water molecules.

Table 2. *The least-squares plane and deviations of atoms*

The average e.s.d. in the atom deviations is 0·011 Å.
Equation of the plane: $-0{\cdot}2810x + 0{\cdot}0005y + 0{\cdot}3067z - 1 = 0$

C(1)	0·015	C(4)	−0·001
C(2)	−0·019	O(11)	0·058
C(3)	0·001		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38070 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Pb—O *distances* (Å) [*calculated by the author from data of Reed* (1959)]

Superscripts refer to trinitroresorcinolate groups in four different positions around the Pb atom.

$O(1^{i})$	2·37	$O(21^{i})$	2·53	$O(2^{ii})$	2·30	$O(31^{ii})$	2·66
$O(11^{iii})$	2·76	$O(1^{iii})$	2·57	$O(31^{iv})$	3·04	$O(32^{iv})$	3·15

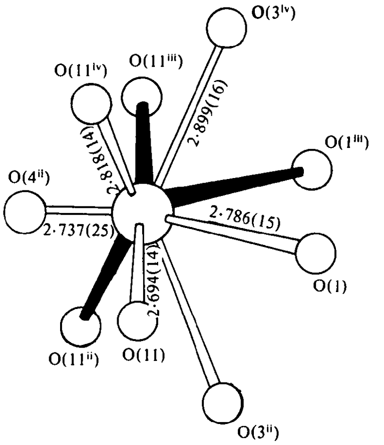

Fig. 3. The coordination of O atoms around the Ba atom. Symmetry code: (i) x,y,z; (ii) $x, \bar{y}, -\frac{1}{2} + z$; (iii) $\bar{x}, y, \frac{1}{2} - z$; (iv) $\bar{x}, \bar{y}, 1 - z$. (Distances are in Å.)

The C(4) nitro group rotates by 58·2° out of the plane of the ring; this rotation is greater than that for the C(2) nitro group which is only 10·2°. This may be attributed to the fact that they are subjected to different force fields from the adjacent O^-, which is electrostatically repelling.

The packing of the two molecules in the unit cell, and the portions of adjacent molecules in neighboring cells, is shown in Fig. 2. The Ba atom is coordinated by nine O atoms: one originates from the water molecule, and the others are from trinitroresorcinolate groups; of these, only four O atoms are independent while the other four are related by the crystallographic twofold axis. Ba—O distances approximately form a homogeneous set, their average being 2·792 (15) Å. Only Ba—$O(3^{iv})$ deviates significantly from the average [by 0·11 (2) Å] (see Fig. 3).

In comparison with N-LTNR, some differences are observed. The nitro groups at C(2), C(4) and C(6) of N-LTNR rotate 38·6, 11·2 and 7·4°, respectively, out of the plane of the benzene ring. In addition, the Pb atom is in a general position and around it are the eight separate O atoms whose distances from Pb (see Table 3) are not as homogeneous as the Ba—O distances in BaTNR. There are four sets of data that deviate significantly from the average, 2·67 Å: Pb—$O(1^{i})$, Pb—$O(2^{ii})$, Pb—$O(31^{iv})$ and Pb—$O(32^{iv})$ by −0·30, −0·37, 0·37 and 0·48 Å, respectively.

All calculations were carried out on a DJS-6 computer by means of a crystal structure computing program written by the author.

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Structures of 2,4,6-Trinitro-1,3-benzenediol $\frac{2}{3}$ Hydrate and 2,4,6-Trinitro-1,3,5-benzenetriol $\frac{2}{3}$ Hydrate

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Abstract. The title compounds, $C_6H_3N_3O_8.\frac{2}{3}H_2O$ (I) and $C_6H_3N_3O_9.\frac{2}{3}H_2O$ (II), are isomorphous, trigonal, space group $P\bar{3}c1$. (I) a = 12·6077 (4), c = 10·1147 (15) Å, U = 1392·37 Å^3, Z = 6, M_r = 257·17, D_c = 1·84, D_m = 1·830 Mg m^{-3}; final R = 0·042 for 582 reflections. (II) a = 13·0699 (10), c = 9·5533 (16) Å, U = 1413·28 Å^3, Z = 6, M_r = 273·17, D_c = 1·925, D_m = 1·913 Mg m^{-3}; final R = 0·041 for