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.

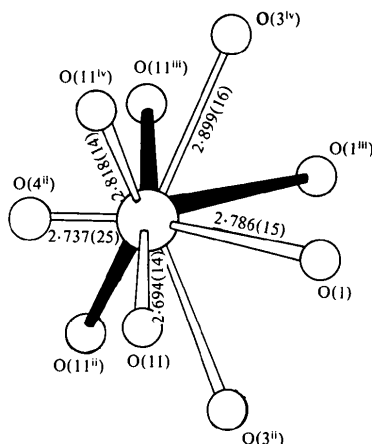|			
O(1^i) 2·37	O(21^i) 2·53	O(2^{ii}) 2·30	O(31^{ii}) 2·66
O(11^{iii}) 2·76	O(1^{iii}) 2·57	O(31^{iv}) 3·04	O(32^{iv}) 3·15

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 ⅔ Hydrate and 2,4,6-Trinitro-1,3,5-benzenetriol ⅔ Hydrate

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Abstract. The title compounds, $C_6H_3N_3O_8 \cdot \frac{2}{3}H_2O$ (I) and $C_6H_3N_3O_9 \cdot \frac{2}{3}H_2O$ (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

954 reflections. In both (I) and (II) the C_6 rings show angular distortion. One nitro group in each structure has a large rotation angle $[67(0\cdot8)$ in I and $63(0\cdot8)°$ in II]. The water molecules are located on the triad axes and are weakly hydrogen-bonded in 'tunnels'.

Introduction. A programme of research is being conducted into the structural properties of primary explosives. Some metal salts of the title compounds, styphnic acid (I) and trinitrophloroglucinol (II), are important primaries and it is of particular interest to investigate the influence of different metals on the structure and the effect this may have on sensitivity and explosive performance. As a basis for this investigation the structures of the parent acids (I) and (II), both efficient secondary explosives in their own right, have been determined. Both (I) and (II) exhibit variable hydration which may be explained by the situation of the water molecules.

Thick, pale-yellow, hexagonal tablets of (I) were grown from Me_2SO solution, and yellow, hexagonal needles of (II) from benzene. Crystal dimensions were $0\cdot2 \times 0\cdot2 \times 0\cdot15$ and $0\cdot25 \times 0\cdot25 \times 0\cdot55$ mm respectively. Data were collected on a Hilger & Watts Y290 four-circle automatic diffractometer, using niobium-filtered Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å). The $\theta-2\theta$ scan technique was applied with a scanning rate of $0\cdot004°$ s^{-1}. Scan ranges varied from $0\cdot4°$ (low θ) to $0\cdot8°$ (high θ) and backgrounds were measured on either side of the peak for half the peak scan time. A complete set of unique reflections was obtained to $2\theta = 44$ (I) and $50°$ (II), and those reflections with $I/\sigma(I) > 2$ were considered observed. At higher angles [to $2\theta = 54$ (I) and $60°$ (II)] reflections were prescanned and only those showing intensities greater than 3σ above background were measured. Every reflection was measured at least twice and the intensities averaged. Of 687 (I) and 1053 (II) unique reflections measured, 570 (I) and 941 (II) were considered observed. In each data collection three standard reflections, monitored at intervals of 50, showed insignificant intensity variations. Only those unobserved reflections calculating greater than measured were included in the structure refinements. Cell parameters were refined by least-squares fit to the reflecting angles of 23 planes ($\theta > 17°$) for (I) and 14 planes ($\theta > 17°$) for (II). Intensities were corrected for Lorentz and polarization effects, but not for absorption [μ(Mo $K\alpha) = 0\cdot165$ (I) and $0\cdot176$ mm^{-1} (II)]. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations, unless otherwise stated, were performed on an IBM 360/195 computer at the Rutherford Appleton Computer Laboratory, using XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

The structure of (I) was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The statistical

distribution of $|E|$ values confirmed a centro-symmetric structure and 203 reflections with $|E| > 1\cdot0$ were used for phase determination. The phase set with the highest figure-of-merit gave the approximate positions of six of the eleven independent non-H atoms. A difference electron-density synthesis indicated the positions of the remaining non-H atoms. Full-matrix least-squares refinements, including anisotropic temperature factors, followed by difference syntheses revealed the H atoms on the acid molecule. These were treated as isotropic and allowed to refine. The aqueous O is located on the triad axis; its H atoms must therefore be in a statistical distribution or else the water molecule is freely rotating. These H atoms were not apparent in the final difference synthesis. The weighting scheme used was $1/(1\cdot909 - 0\cdot104F_{obs} + 0\cdot0022F^2_{obs})$. Final R was $0\cdot042$ (582 reflections); $R_w = 0\cdot045$.

The positions of the non-H atoms from (I) were used as a starting point for the solution of (II). A difference synthesis indicated the position of the remaining O atom and the non-aqueous H atoms. This hydroxyl O is on a twofold axis and so its H atom takes up two equivalent positions. It was therefore refined as having a population parameter of $0\cdot5$. Refinement of the structure proceeded as for (I), but two reflections, 202 and 213, were judged to be suffering from extinction and were omitted. The weighting scheme used was $1/(1\cdot817 - 0\cdot119F_{obs} + 0\cdot0026F^2_{obs})$. The final R value was $0\cdot041$ (954 reflections); $R_w = 0\cdot044$.

Discussion. Atomic parameters are given in Table 1 (I) and Table 2 (II).* Fig. 1 illustrates a molecule of (I)

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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 38065 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$ *for* C, N, O; $\times 10^3$ *for* H) *and isotropic thermal parameters* (Å^2 $\times 10^3$) *for* (I), $C_6H_3N_3O_8.\frac{2}{3}H_2O$

	x	y	z	U^*_{eq} or U_{iso} (H)
O(3)	6667	3333	1047 (5)	84
O(1)	3597 (2)	5268 (2)	1090 (3)	49
N(1)	1269 (2)	2959 (3)	938 (2)	41
O(11)	324 (2)	1976 (2)	983 (2)	47
O(12)	1402 (2)	3810 (2)	221 (2)	52
N(2)	5514 (3)	5514 (3)	2500	36
O(21)	5528 (2)	6400 (2)	2998 (2)	50
C(1)	3388 (3)	4272 (3)	1748 (3)	34
C(2)	2297 (3)	3140 (3)	1755 (3)	32
C(3)	2180 (4)	2180 (4)	2500	33
C(6)	4350 (3)	4350 (3)	2500	30
H(1)	147 (4)	147 (4)	250	20 (13)
H(2)	305 (4)	509 (4)	52 (4)	45 (14)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

indicating atomic numbering and the important bond distances and angles. The molecule is bisected by the twofold axis. Trinitrophloroglucinol (II) is similarly illustrated in Fig. 2.

Table 2. *Positional parameters* ($\times 10^4$ *for* C, N, O; $\times 10^3$ *for* H) *and isotropic thermal parameters* (Å^2 $\times 10^3$) *for* (II), $C_6H_3N_3O_9 \cdot \frac{2}{3}H_2O$

	x	y	z	U_{eq}^* or U_{iso} (H)
O(3)	6667	3333	1083 (4)	73
O(1)	3638 (2)	5311 (2)	1112 (2)	41
O(2)	1264 (2)	1264 (2)	2500	37
N(1)	1427 (2)	3139 (2)	896 (2)	31
O(11)	465 (2)	2226 (2)	919 (2)	40
O(12)	1597 (2)	3977 (2)	131 (2)	42
N(2)	5520 (2)	5520 (2)	2500	29
O(21)	5530 (2)	6378 (2)	3021 (2)	45
C(1)	3457 (2)	4337 (2)	1762 (2)	27
C(2)	2385 (2)	3252 (2)	1744 (2)	26
C(3)	2266 (2)	2266 (2)	2500	25
C(6)	4399 (2)	4399 (2)	2500	25
H(1)	301 (3)	515 (3)	42 (4)	71 (12)
H(2)	77 (5)	136 (5)	202 (5)	18 (15)

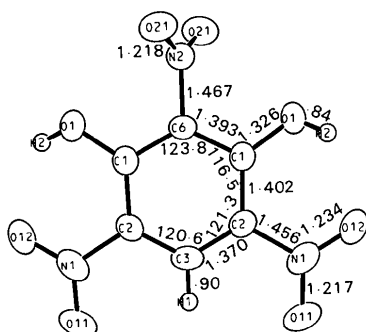$* \ U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Fig. 1. View of a molecule of (I) showing atom numbering with bond lengths (Å) and angles (°). E.s.d.'s range from 0·003–0·005 Å and from 0·2–0·3° for non-H interactions. E.s.d.'s for O(1)–H(2) and C(3)–H(1) are 0·04 and 0·03 Å, respectively.
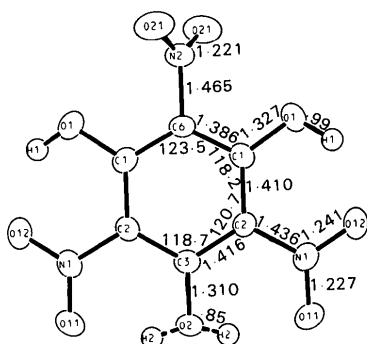

Fig. 2. View of a molecule of (II) showing atom numbering with bond lengths (Å) and angles (°). E.s.d.'s range from 0·002–0·004 Å and from 0·15–0·2° for non-H interactions. E.s.d.'s for O(1)–H(1) and O(2)–H(2) are 0·04 and 0·07 Å, respectively.

The geometry of the carbon skeleton in substituted benzene derivatives is known to be sensitive to the electronic properties of the substituents (Domenicano, Vaciago & Coulson, 1975; Domenicano & Murray-Rust, 1979; Holden & Dickinson, 1977; Katritzky & Topsom, 1970). Electron-withdrawing substituents such as $-NO_2$ tend to increase the internal angle at the *ipso* carbon and shorten the adjacent C—C bonds. The opposite effect occurs with electron-releasing groups. It is found that angular variations are generally more reliable than bond lengths. Most of the correlations have been drawn from mono- and di-substituted compounds; when more than one substituent is present each can exert its normal influence and in addition there is the possibility of through-conjugation leading to further π-distortions. In the presence of conjugation the bond to the substituent tends to be shorter, the adjacent C—C bonds longer and the angle at the *ipso* carbon smaller than in the absence of conjugation, regardless of the electronegativity of the substituent.

The bond lengths and angles in (I) and (II) follow the predicted pattern, with an increase in the internal ring angles at the nitro groups and a decrease at the hydroxyls. The ring is planar [maximum deviation of 0·01 (1) Å for both I and II] and the sum of the internal ring angles is 720° in each molecule. In both cases the largest angle is at C(6). The nitro group here is twisted by 67(0·8) (I) and 63(0·8)° (II) out of the plane of the ring and is probably acting essentially as an unconjugated group. The remaining nitro group is expected to show more conjugation with the ring as the rotation about the C(2)—N(1) bond is very much less [3·7(0·7) (I) and 7(0·6)° (II)]. The internal angles here do show the expected decrease and in (II) the C(2)—N(1) bond is significantly shortened.

The average C—C bond distances, 1·388 (I) and 1·405 Å (II), are not very different from those found in benzene. The larger value for (II) is not unreasonable owing to the increased substitution and increased probability of conjugation.

The C(1)—O(1) bond length [1·326 (I) and 1·327 Å (II)] is a little shorter than found in unconjugated phenols, normally about 1·36 Å (*Molecular Structures and Dimensions*, 1972). In (II) C(3)—O(2) is considerably shorter at 1·310 Å, and this, together with the pattern of neighbouring bond distances and angles, indicates some delocalization of the oxygen lone pair of electrons onto the adjacent nitro groups.

Fig. 3 illustrates the packing arrangement within a unit cell of (I); (II) is very similar. Because the molecules are situated along the twofold axes the net effect is to leave 'tunnels' along the threefold axes. It is here that the water of crystallization is found, weakly hydrogen-bonded to the surrounding O atoms. This situation probably explains the variability in hydration found for these compounds. The large rotation of the nitro group at C(6) minimizes both inter- and intra-
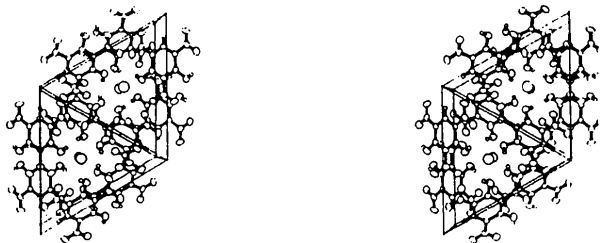
Fig. 3. Stereoscopic packing arrangement within a unit cell of (I), viewed along **c**. Thermal ellipsoids enclose 50% probability (Johnson, 1976).

Table 3. *Hydrogen-bond distances* (Å)

(I) $C_6H_3N_3O_8 \cdot \frac{3}{4}H_2O$

O(1)[H(2)]···O(12)	2·592 (3)	(3×) O(1)···O(3^i)	2·911 (5)
[O(1)]H(2)···O(12)	1·91 (4)	(3×) O(21)···O(3^{ii})	3·104 (3)

(II) $C_6H_3N_3O_9 \cdot \frac{3}{4}H_2O$

O(1)[H(1)]···O(12)	2·527 (3)	(3×) O(1)···O(3^i)	2·898 (4)
O(2)[H(2)]···O(11)	2·503 (3)	(3×) O(21)···O(3^{ii})	3·194 (4)
[O(1)]H(1)···O(12)	1·74 (3)		
[O(2)]H(2)···O(11)	1·73 (7)		

Symmetry code: (i) $1 - x, 1 - y, -z; y, 1 + y - x, -z; x - y, x, -z;$
(ii) $y, x, \frac{1}{2} - z; x - y, 1 - y, \frac{1}{2} - z; 1 - x, 1 + y - x, \frac{1}{2} - z.$

molecular steric interference and allows hydrogen bonding to the water molecule.

Table 3 gives some hydrogen-bond distances. Both (I) and (II) show intramolecular hydrogen bonding

between the O(1) hydroxyl group and the N(1) nitro group *via* O(12). In addition, in (II) O(2) is hydrogen-bonded to the same nitro group *via* O(11). The water O(3) is weakly hydrogen-bonded to the three phenoxide O atoms [O(1)] and three nitro O atoms [O(21)] that surround it.

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Structures of the Barium Salt of 2,4,6-Trinitro-1,3-benzenediol Monohydrate and the Isomorphous Lead Salt (β-Polymorph)

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Abstract. The title compounds, $C_6HN_3O_8^{2-} \cdot Ba^{2+} \cdot H_2O$ (I) and β-$C_6HN_3O_8^{2-} \cdot Pb^{2+} \cdot H_2O$ (II), are isomorphous, monoclinic, space group $P2/c$. (I) $a = 7·5390$ (5), $b = 8·0876$ (7), $c = 8·7555$ (6) Å, $\beta = 106·551$ (6)°, $U = 511·72$ Å³, $M_r = 398·44$, $Z = 2$, $D_c = 2·59$ Mg m⁻³. Final $R = 0·028$ for 2401 reflections. (II) $a = 7·519$ (2), $b = 8·004$ (2), $c = 8·413$ (2) Å, $\beta = 107·22$ (2)°, $U = 483·62$ Å³, $M_r = 468·29$, $Z = 2$, $D_c = 3·22$ Mg m⁻³. Final $R = 0·050$ for 1541 reflections. In both structures the benzene ring is distorted; internal angles range from 112·6 (2) to 128·4 (3)° (I) and from 113·1 (8) to 126·9 (11)° (II); C—C bond lengths vary from

1·384 (2) to 1·446 (3) Å (I) and from 1·38 (1) to 1·43 (1) Å (II). In (I) the ring is significantly nonplanar. The nitro groups are twisted relative to the mean planes of the rings, one of them being rotated by 62(1)° in each compound. The metal atoms are nine-coordinate and linked in chains *via* oxygen bridges.

Introduction. 2,4,6-Trinitro-1,3-benzenediol (styphnic acid) and its metal salts are important military and commerical explosives. The lead salts in particular are widely used as primary explosives and in detonators, and both the normal and basic salts exhibit poly-