

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) $C_6H_3N_3O_8 \cdot \frac{1}{2}H_2O$			
O(1)[H(2)]...O(12)	2.592 (3)	(3×) O(1)...O(3 <sup>l</sup> )	2.911 (5)
[O(1)]H(2)...O(12)	1.91 (4)	(3×) O(21)...O(3 <sup>h</sup> )	3.104 (3)
(II) $C_6H_3N_3O_9 \cdot \frac{2}{3}H_2O$			
O(1)[H(1)]...O(12)	2.527 (3)	(3×) O(1)...O(3 <sup>l</sup> )	2.898 (4)
O(2)[H(2)]...O(11)	2.503 (3)	(3×) O(21)...O(3 <sup>h</sup> )	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 ( $\beta$ -Polymorph)

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**Abstract.** The title compounds,  $C_6HN_3O_8^{2-} \cdot Ba^{2+} \cdot H_2O$  (I) and  $\beta$ - $C_6HN_3O_8^{2-} \cdot Pb^{2+} \cdot H_2O$  (II), are isomorphous, monoclinic, space group  $P2_1/c$ . (I)  $a = 7.5390$  (5),  $b = 8.0876$  (7),  $c = 8.7555$  (6) Å,  $\beta = 106.551$  (6)°,  $U = 511.72$  Å<sup>3</sup>,  $M_r = 398.44$ ,  $Z = 2$ ,  $D_c = 2.59$  Mg m<sup>-3</sup>. 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)°,  $U = 483.62$  Å<sup>3</sup>,  $M_r = 468.29$ ,  $Z = 2$ ,  $D_c = 3.22$  Mg m<sup>-3</sup>. 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 non-planar. 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 commercial explosives. The lead salts in particular are widely used as primary explosives and in detonators, and both the normal and basic salts exhibit poly-

morphism. Considering their importance remarkably little is known about the nature of these compounds. Structure determinations have been carried out on the title compounds as part of a programme of research into the structural properties of primary explosives. It is of particular interest to investigate any correlations between molecular geometry and sensitivity in these compounds.

Barium styphnate was prepared from barium acetate and freshly prepared magnesium styphnate in nitric acid solution at 348 K (Taylor, Thomas & Holloway, 1955). Lead styphnate was prepared by mixing solutions of lead nitrate and freshly prepared magnesium styphnate at 313 K in the presence of sorbitan monooleate (Taylor & White, 1949). Both compounds have low solubility, and suitable crystals were grown from the mother liquors. Lead styphnate is formed as yellow crystals with a platy habit. The crystal chosen for diffractometry, however, was a well-formed parallelepiped of approximate dimensions  $0.12 \times 0.08 \times 0.08$  mm. The barium styphnate crystal was similar in shape and size.

The measurement of intensity data from both crystals was carried out on a Hilger & Watts Y290 four-circle automatic diffractometer, with niobium-filtered Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). The  $\theta-2\theta$  scan technique was applied with a scanning rate of  $0.004^\circ s^{-1}$ . Scan ranges varied from  $0.5$  (low  $\theta$ ) to  $0.75^\circ$  (high  $\theta$ ) 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  $2\theta = 52^\circ$ . At higher angles [to  $2\theta = 76$  (I) and  $70^\circ$  (II)] reflections were prescanned and only those showing intensities greater than  $3\sigma$  above background were measured. Every reflection was measured at least twice and the intensities averaged. Of 2525 (I) and 1661 (II) unique reflections measured, 2356 (I) and 1505 (II) were considered observed. In each data collection three standard reflections, monitored at intervals of 50, showed insignificant intensity variations. Intensities were corrected for Lorentz and polarization effects and also for absorption [ $\mu(\text{Mo } K\alpha) = 3.93$  (I) and  $17.64 \text{ mm}^{-1}$  (II)], using the method of Alcock (1970). Accurate cell parameters for both compounds were obtained by least-squares fit to the reflecting angles of 14 reflections ( $2\theta > 40^\circ$ ).

Systematic extinctions ( $h0l$ ;  $l = 2n$ ) indicate space groups  $Pc$  or  $P2/c$ . The non-centrosymmetric cell was initially chosen but subsequently changed to  $P2/c$  on the basis of improved refinement.

In each case the positions of all non-H atoms were readily located by the heavy-atom method. Least-squares refinement proceeded routinely with anisotropic temperature factors applied to all atoms in the final cycles. H atoms were clearly visible in the difference map of the barium salt and were included in the final refinement (assumed isotropic).

The weighting scheme for both refinements was based on  $w = 1.0/(A + DF_{\text{obs}} + EF_{\text{obs}}^2)$ , which was adjusted to make the average  $w\Delta^2$  independent of  $F_{\text{obs}}$ . The values of  $A$ ,  $D$  and  $E$  used were  $3.10$ ,  $-0.166$  and  $0.0025$  for (I) and  $10.36$ ,  $-0.4066$  and  $0.0057$  for (II). Reflections 012 and  $20\bar{2}$  (I) and  $20\bar{2}$  (II) were judged to be suffering from extinction and omitted from the final refinement. Final  $R$  values were 0.028 (2401 reflections) for (I);  $R_w = 0.028$ ; and 0.050 (1541 reflections) for (II);  $R_w = 0.058$ . Atomic scattering factors (metal atoms assumed ionic) and anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed at the Rutherford Appleton Computer Laboratory with XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

**Discussion.** Final atomic parameters are given in Table 1.\* The interatomic distances and angles are in Table 2 and the atom-numbering scheme is illustrated in Fig. 1.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38066 (22 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 H  $\times 10^3$ ) with *e.s.d.*'s and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^*$ or $U_{\text{iso}}(\text{H})$
(I) $C_6HN_3O_8^{2-} \cdot Ba^{2+} \cdot H_2O$				
Ba	0	-642.4 (3)	7500	14
O(3)†	0	2722 (4)	7500	28
O(1)	2126 (2)	525 (2)	5535 (3)	17
O(11)	2749 (3)	5636 (3)	5113 (3)	34
O(12)	1016 (3)	3542 (3)	4242 (2)	26
O(31)	3707 (3)	-1920 (3)	7798 (3)	27
N(1)	2398 (3)	4152 (2)	5184 (2)	18
N(3)	5000	-1188 (3)	7500	15
C(1)	3459 (3)	1368 (3)	6394 (2)	14
C(2)	3634 (3)	3148 (3)	6366 (2)	15
C(3)	5000	3979 (4)	7500	17
C(6)	5000	602 (4)	7500	15
H(1)	500	523 (8)	750	16 (15)
H(2)	70 (10)	327 (9)	805 (8)	21 (20)
(II) $\beta-C_6HN_3O_8^{2-} \cdot Pb^{2+} \cdot H_2O$				
Pb	0	-573 (1)	7500	18
O(3)†	0	2543 (14)	7500	28
O(1)	2041 (9)	376 (10)	5518 (9)	21
O(11)	2716 (11)	5524 (11)	4982 (11)	29
O(12)	802 (10)	3463 (11)	4282 (10)	25
O(31)	3735 (10)	-2068 (10)	7847 (11)	30
N(1)	2296 (10)	4062 (10)	5146 (10)	18
N(3)	5000	-1333 (13)	7500	16
C(1)	3422 (11)	1259 (11)	6388 (10)	15
C(2)	3600 (11)	3027 (12)	6352 (10)	15
C(3)	5000	3882 (17)	7500	18
C(6)	5000	463 (17)	7500	13

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

† O(3) is water oxygen.

Table 2. *Interatomic distances (Å) and angles (°) in the anions with e.s.d.'s in parentheses*

	Barium stypnate	$\beta$ -Lead stypnate
(a) Distances		
C(1)—C(2)	1.446 (3)	1.42 (1)
C(2)—C(3)	1.384 (2)	1.38 (1)
C(1)—C(6)	1.425 (2)	1.43 (1)
C(1)—O(1)	1.269 (2)	1.29 (1)
C(2)—N(1)	1.431 (3)	1.45 (1)
C(6)—N(3)	1.447 (4)	1.44 (2)
N(1)—O(11)	1.234 (3)	1.23 (1)
N(1)—O(12)	1.232 (3)	1.24 (1)
N(3)—O(31)	1.230 (3)	1.22 (1)
(b) Angles		
C(6)—C(1)—C(2)	112.6 (2)	113.1 (8)
C(1)—C(2)—C(3)	121.6 (2)	122.4 (8)
C(2)—C(3)—C(2')	121.9 (2)	120.6 (11)
C(1')—C(6)—C(1)	128.4 (3)	126.9 (11)
C(2)—C(1)—O(1)	125.8 (2)	126.8 (7)
C(6)—C(1)—O(1)	121.6 (2)	120.1 (9)
C(1)—C(2)—N(1)	122.2 (2)	122.5 (7)
C(3)—C(2)—N(1)	116.2 (2)	115.1 (8)
C(1)—C(6)—N(3)	115.8 (2)	116.5 (6)
C(2)—N(1)—O(11)	118.9 (2)	118.7 (7)
C(2)—N(1)—O(12)	120.6 (2)	119.9 (8)
O(31)—N(3)—O(31')	122.5 (3)	122.6 (10)
C(6)—N(3)—O(31)	118.8 (2)	118.7 (6)

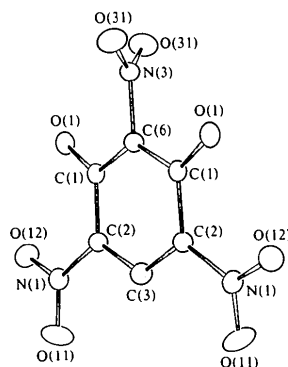


Fig. 1. Perspective view of the styphnate ion in (I), showing the atom-numbering scheme. Thermal ellipsoids enclose 50% probability (Johnson, 1976).

The molecule is bisected by the twofold axis. The two analyses of the styphnate ion are in good agreement.

The bond lengths and angles in the carbon hexagon of the styphnate ions are quite variable and follow the predicted trends (Pierce-Butler, 1982, and references therein; Carter, McPhail & Sim, 1966; Domenicano & Vacigo, 1979). The structure of the parent acid has been reported (Pierce-Butler, 1982), which shows similar distortions to other purely organic substituted benzenes (e.g. Domenicano & Murray-Rust, 1979; Bailey & Prout, 1965; Eliel, Koskimies, McPhail & Swern, 1976). It is apparent that substituent effects are much greater in the ion for both bond angles and bond

lengths. The largest ring angles, 128.4 (I) and 126.9° (II), are at C(6) and coincide with the position of the nitro group with the greatest angle of rotation [62(1)° for both compounds]. This nitro group is probably acting as if unconjugated. The remaining nitro groups, at C(2), have much smaller rotation angles [11(0.7) (I) and 16(1)° (II)] and might be expected to be involved in conjugation with the ring. The internal ring angles at C(2) of 121.6 (I) and 122.4° (II) support this.

The C(1)—O(1) bond lengths of 1.269 (I) and 1.29 Å (II) are considerably shorter than 1.326 Å found in the parent acid, and 1.36 Å expected for a single bond (*Molecular Structures and Dimensions*, 1972). This indicates extensive delocalization of the ionic charge onto the ring. The internal angles at C(1) are very small, 112.6 (I) and 113.1° (II), as expected from the combination of effects due to an electron-releasing substituent involved in substantial conjugation.

The C—C bond-length variations also follow the predicted pattern and again the effects are much greater than normally found in substituted benzenes, individual values varying from 1.384 to 1.446 Å (I) and 1.38 to 1.43 Å (II). The average C—C bond lengths [1.418 (I) and 1.41 Å (II)] are larger than in styphnic acid (1.388 Å). This may be explained by the increased electron density due to delocalization of the charge around the ring. Similar effects on both bond lengths and angles have been observed in potassium and ammonium picrates (Maartmann-Moe, 1969; Palenik, 1972).

The least-squares planes of the rings were calculated using all six C atoms. The deviations of individual atoms, shown in Table 3, are very similar for the two compounds and indicate a departure from planarity, particularly significant for (I). The rings adopt a boat-type conformation with a maximum dihedral angle of 14°. They may be considered to be twisted about the twofold axis, with an angle of approximately 5.5°.

The nitro groups are all rotated relative to the mean planes of the benzene rings (see above). Similar rotations have been observed in other nitroaromatics.

Table 3. *Least-squares planes*

(a) Barium salt							
Equation of the mean plane of the ring C(1)—C(6) is							
$-5.68937x - 0.00111y + 7.388857z = 1.84611$							
Distances of atoms from plane (Å) (e.s.d.'s ~0.003)							
C(1)	C(2)	C(3)	C(6)	O(1)	N(1)	N(3)	
-0.0586	0.0618	0.0001	0.0005	-0.1827	0.2325	0.0007	
(b) $\beta$ -Lead salt							
Equation of the mean plane of the ring C(1)—C(6) is							
$-5.50668x + 0.00209y + 7.29556z = 1.82679$							
Distances of atoms from plane (Å) (e.s.d.'s ~0.01)							
C(1)	C(2)	C(3)	C(6)	O(1)	N(1)	N(3)	
-0.0596	0.0649	-0.001	-0.002	-0.185	0.227	-0.002	

Holden & Dickinson (1977) found no correlation between the C–N bond length and the angle of rotation of the  $-\text{NO}_2$  group, and concluded that there is a restoring force towards coplanarity with the ring. Steric factors are obviously important and bulky *ortho* substituents tend to produce larger rotation angles. Some examples are trinitrotoluene ( $59^\circ$  max.) and hexanitrostilbene ( $48^\circ$  max.) (Duke, private communication, undated); *N*-methyl-2,4,6-trinitroacetanilide ( $54^\circ$  max.) (Cristoph & Fleischer, 1973); 2,4,6-trinitro-*m*-xylene ( $76^\circ$  max.) (Bryden, 1972) and 2,4,6-trinitro-1,3-benzenediol, styphnic acid ( $67^\circ$  max.) (Pierce-Butler, 1982). However, nitro groups can be quite flat in highly substituted systems, e.g. 2,4,6-trinitro-1,3,5-benzenetriamine ( $4^\circ$  max.) (Cady & Larson, 1965) and yet still be somewhat twisted when steric crowding by *ortho* substituents cannot be the cause, as in *p*-dinitrobenzene ( $10.2^\circ$ ) (Di Rienzo, Domenicano & Riva di Sanseverino, 1980). In (I) and (II) the large rotation angle of  $62^\circ$  allows the nitro O atoms to come within the coordination sphere of the metal ion.

The shortest metal–O distances are listed in Table 4. The metals exhibit nine-coordination and may be regarded as having distorted tricapped trigonal prismatic geometry. The polyhedra are approximately pentagonal bipyramidal, with apices occupied by pairs of O atoms perpendicular to each other. Fig. 2 illustrates the coordination of the Ba atom; the Pb atom

Table 4. *Metal–O distances (Å) with e.s.d.'s in parentheses*

$C_6HN_3O_8^{2-} \cdot Ba^{2+} \cdot H_2O$		$\beta\text{-}C_6HN_3O_8^{2-} \cdot Pb^{2+} \cdot H_2O$	
Ba–O(3)*	2.721 (3)	Pb–O(3)*	2.494 (11)
(2×) Ba–O(1 <sup>l</sup> )	2.686 (1)	(2×) Pb–O(1 <sup>l</sup> )	2.554 (7)
(2×) Ba–O(1 <sup>ll</sup> )	2.827 (2)	(2×) Pb–O(1 <sup>ll</sup> )	2.689 (8)
(2×) Ba–O(12 <sup>ll</sup> )	2.784 (2)	(2×) Pb–O(12 <sup>ll</sup> )	2.725 (8)
(2×) Ba–O(31 <sup>l</sup> )	2.921 (2)	(2×) Pb–O(31 <sup>l</sup> )	2.987 (8)

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

\* O(3) is water oxygen.

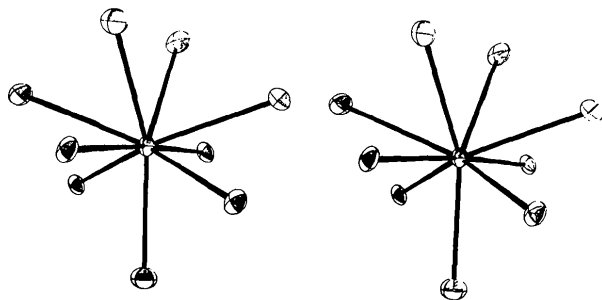


Fig. 2. A stereoview showing the coordination of the barium ion in (I). Thermal ellipsoids enclose 50% probability (Johnson, 1976).

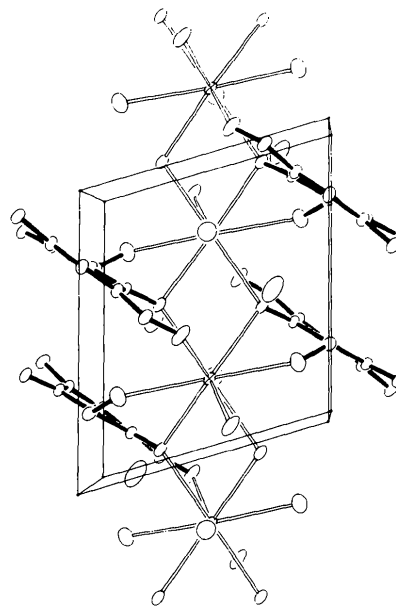


Fig. 3. The packing arrangement within a unit cell of (II) viewed along *b*.

is similar. In (I) the five shortest Ba–O distances lie in the equatorial plane. The metal–O distances are similar to the sums of the appropriate ionic radii;  $Ba^{2+} + O^{2-} = 2.87 \text{ \AA}$ ;  $Pb^{2+} + O^{2-} = 2.75 \text{ \AA}$  (Shannon, 1976) although some of the Pb–O interactions are rather short, possibly indicating some degree of covalency.

The metals are linked *via* oxygen bridges in infinite chains parallel to *c*. The styphnate ions are aligned in parallel planes. The packing arrangement within a unit cell of (II) is illustrated in Fig. 3.

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*Note added in proof:* Whilst this paper was in the press the work of Du (1982) on the structure of barium styphnate (named resorcinolate) was brought to the author's attention. The two versions of the structure are very similar with cell constants, positional parameters and most of the derived quantities varying by no more than twice Du's standard deviations. The larger differences seem to be associated with those atoms on or close to the crystallographic twofold axis. Overall, the greatest difference appears to be in the planarity of the ring. This work shows the atom deviations to be larger and more significant than Du found. The differences are due in part to the better definition of atomic parameters, as more data were used in the refinement, and also to the inclusion of the symmetry-related C atoms in the calculation of the least-squares plane.

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