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The Crystallography of Nitramine–Solvent Complexes. VI.* Structure of the 1:1 Molecular Complex Formed between 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) and 4-Hydroxybutanoic Acid Lactone

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Abstract. $C_8H_{14}N_6O_{10} \cdot C_4H_6O_2$, $M_r = 440.3$, monoclinic, $P2_1/c$, $a = 14.966$ (3), $b = 6.594$ (1), $c = 20.792$ (5) Å, $\beta = 106.77$ (2)°, $Z = 4$, $D_x = 1.488$, $D_m = 1.49$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 1.063$ mm⁻¹, $F(000) = 920$, $T = 293$ K, $R = 0.075$ for 3349 observed reflexions. Molecules of BSX form centrosymmetric dimers, weakly bound by N...O interactions [2.951 (4) and 3.096 (4) Å]; the solvent molecules are bound by similar interactions to the dimers. This structural entity (two BSX and two solvent molecules) resembles that found in the other two types

of BSX complex reported previously. The three types differ in the modes of packing of the weakly bound units. The 4-hydroxybutanoic acid lactone molecule is positionally disordered (0.65/0.35) between two orientations.

Introduction. 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) forms complexes with a wide variety of organic solvents and the complexes can be divided into four distinct types (*A*, *B*, *C* or *D*) within each of which the cell dimensions are similar and the internal symmetry the same (Cobbedick & Small, 1973a). The structures of the type *A* complex formed with *N,N*-dimethylformamide, BSX–DMF (Cobbedick & Small, 1973b), the type *C* complex formed with 1,4-dioxane, BSX–DOX (Cobbedick & Small, 1973c) and the

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structure of pure BSX (Cobbledick & Small, 1973*d*) have been described. The type *B* complex formed with 4-hydroxybutanoic acid lactone (BSX-BL) was selected for a structure determination.

Experimental. Colourless needles (obtained by recrystallizing BSX from 4-hydroxybutanoic acid lactone at room temperature), $0.5 \times 0.3 \times 0.3$ mm. Density measured by flotation. Manually set four-circle diffractometer (Small & Travers, 1961), Ni-filtered Cu $K\alpha$ radiation. Cell dimensions by least squares using 50 measured θ values. 4371 unique reflexions, $\theta_{\max} 82^\circ$, $h-18 \rightarrow 18$, $k 0 \rightarrow 8$, $l 0 \rightarrow 26$, standard every 20 reflexions, variation $< 1\%$. Using 3349 reflexions, absorption-corrected using the program *ABSCOR* of *XRAY63* (Stewart, 1964), with $I > \sigma(I)$, structure solved using an early version of *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix refinement (on F) with anisotropic temperature factors except isotropic H. $F_o - F_c$ map revealed H which were included, but not refined, at calculated positions ($C-H = 1.08$ Å).

With its atoms freely refined the solvent molecule was highly distorted with additional unaccounted for electron-density features (R was 0.098). A positionally disordered model with two displaced rigidly constrained molecules (0.65 and 0.35 site occupation) was more successful with $R = 0.075$ and the shifts/e.s.d. 0.14 for the BSX molecule and 0.3 for the solvent. The largest features on the final $F_o - F_c$ map were $0.4 \text{ e } \text{\AA}^{-3}$ in the region of the solvent atoms indicating that the disorder was still imperfectly accounted for. A weighting scheme $w = 0.8535/[\sigma^2(F) + 0.006025 F^2]$ was used, $wR = 0.093$. The dimensions of the constrained model used for the 4-hydroxybutanoic acid lactone (γ -butyrolactone) are shown in Fig. 1(*a*); they are based on those found in 2-phenoxy- γ -butyrolactone (Lere-Porte, Petrissans & Brianso, 1981). The relation between the two disordered molecules is shown in Fig. 1(*b*).

Refinement of the structure was carried out with *SHELX76* (Sheldrick, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography*

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\text{\AA}^2 \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
C(1)	1477 (2)	3258 (5)	2591 (1)	668
C(2)	2625 (2)	5865 (5)	2844 (1)	662
C(3)	2731 (2)	6133 (4)	4093 (1)	484
C(4)	3770 (2)	7946 (4)	5134 (1)	488
C(5)	3573 (2)	10345 (4)	6044 (1)	646
C(6)	5167 (2)	10152 (4)	6671 (1)	595
C(7)	1176 (3)	1380 (6)	2185 (2)	862
C(8)	5823 (2)	9835 (5)	7360 (2)	708
N(1)	3124 (2)	5668 (4)	3548 (1)	550
N(2)	4020 (2)	5032 (4)	3710 (1)	647
N(3)	3109 (1)	7946 (3)	4467 (1)	477
N(4)	2842 (2)	9762 (3)	4177 (1)	577
N(5)	3366 (2)	8501 (4)	5664 (1)	579
N(6)	2872 (2)	7036 (5)	5881 (1)	687
O(1)	2312 (2)	3932 (3)	2538 (1)	668
O(2)	4354 (2)	4652 (5)	3255 (1)	957
O(3)	4441 (1)	4922 (4)	4312 (1)	733
O(4)	2320 (2)	9759 (3)	3598 (1)	727
O(5)	3132 (2)	11280 (3)	4507 (1)	748
O(6)	2773 (2)	5411 (4)	5588 (1)	891
O(7)	2577 (2)	7448 (5)	6354 (1)	948
O(8)	4273 (1)	10038 (3)	6677 (1)	631
O(9)	1066 (2)	4124 (5)	2917 (2)	947
O(10)	5382 (2)	10457 (4)	6169 (1)	812
C(10)	588 (2)	-320 (4)	4305 (2)	1065
C(11)	-84 (2)	1197 (4)	3863 (2)	1125
C(9)	74 (2)	3133 (4)	4280 (2)	867
C(12)	1008 (2)	2784 (4)	4813 (2)	1336
O(11)	1074 (2)	550 (4)	4880 (2)	1235
O(12)	653 (2)	-2111 (4)	4207 (2)	1512
C(13)	872 (3)	12 (8)	4552 (3)	1523
C(14)	31 (3)	-166 (8)	3936 (3)	909
C(15)	-296 (3)	2007 (8)	3779 (3)	1692
C(16)	176 (3)	3160 (8)	4420 (3)	2062
O(13)	1019 (3)	1943 (8)	4737 (3)	2051
O(14)	1357 (3)	-1337 (8)	4850 (3)	1329

$$*U_{eq} = \frac{1}{3} \sin^2 \beta (U_{11} + U_{22} \sin^2 \beta + U_{33} + U_{13} \cos \beta).$$

(1962) were used. The final coordinates are given in Table 1.*

Discussion. The BSX molecule is shown in Fig. 3, a view of the unit-cell contents is shown in Fig. 4. Bond distances and angles, Fig. 2, are very similar to those found in BSX (Cobbledick & Small, 1973*d*), BSX-DMF (Cobbledick & Small, 1973*b*) and BSX-DOX (Cobbledick & Small, 1973*c*). The torsion angles along the chain (Table 2) show a marked similarity in the three complexes; pure BSX is different with a relative rotation of the acetyl groups by approximately 40° . It appears, therefore, that molecular packing has relatively little effect upon the shape of the BSX molecule in the central region around the nitramine groups. There are several short intramolecular $O \cdots H$ distances ($2.33-2.51$ Å). Intramolecular $C-H \cdots O$ hydrogen bonding has been postulated in similar nitramine compounds (Choi & Boutin, 1970; Choi & Prince, 1972) but the deviation from linearity precludes the interpretation of the close $C \cdots O$ and $H \cdots O$ distances

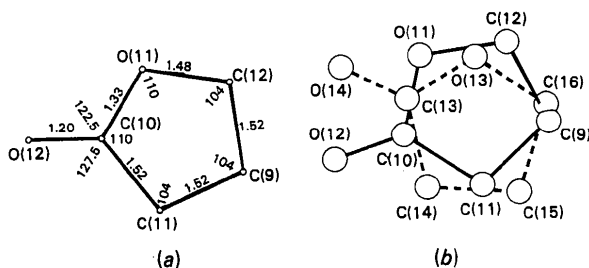


Fig. 1. (*a*) Dimensions (\AA , $^\circ$) assumed for 4-hydroxybutanoic acid lactone (BL). (*b*) Relation between the two disordered molecules of BL.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43816 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in BSX as hydrogen bonds. The chain of atoms between O(1) and O(8) lies approximately around a threefold screw axis and the three almost planar nitramine groups are evenly spaced in planes approximately 120° apart. Repulsion effects between these groups may be predominant in determining the relatively fixed conformation of the BSX molecule. In the

Table 2. *Torsion angles* ($^\circ$)

C(1)–O(1)–C(2)–N(1)	85.9 (4)	N(4)–N(3)–C(4)–N(5)	75.3 (3)
O(1)–C(2)–N(1)–N(2)	78.3 (3)	N(3)–C(4)–N(5)–N(6)	79.0 (3)
N(2)–N(1)–C(3)–N(3)	70.0 (3)	N(6)–N(5)–C(5)–O(8)	72.0 (3)
N(1)–C(3)–N(3)–N(4)	74.0 (3)	N(5)–C(5)–O(8)–C(6)	85.5 (3)

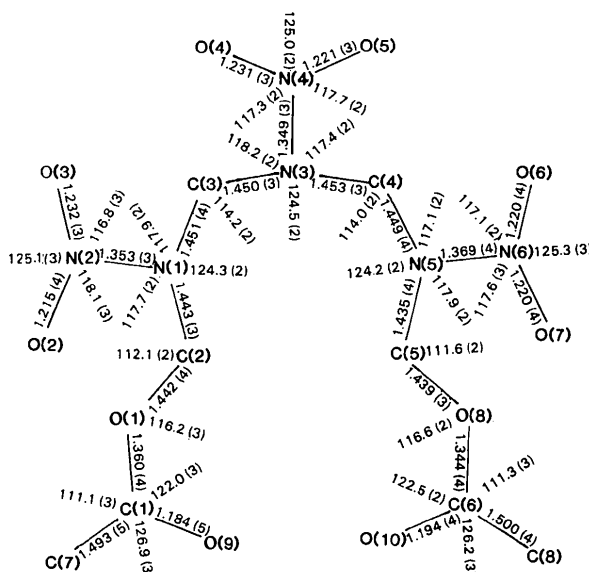
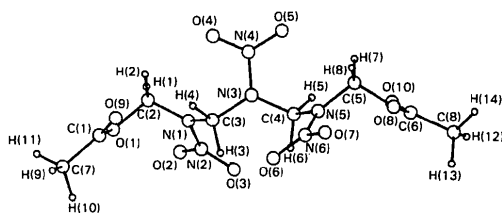
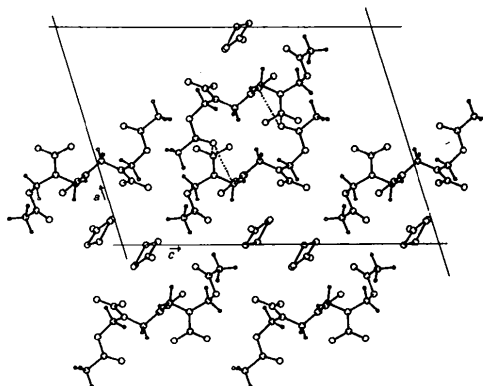
Fig. 2. Bond distances (Å) and angles ($^\circ$) in BSX (diagrammatic).

Fig. 3. Conformation of BSX.

Fig. 4. Projection of the unit cell along *b*.

complexed structures, the BSX molecules have approximate twofold symmetry about the central N(3)–N(4) bond; in pure BSX an exact twofold axis is a space-group requirement.

The carbonyl O of one BSX molecule interacts with the N atoms of two adjacent nitro groups in a centrosymmetrically related BSX molecule to give dimer units. Similar dimers occur in the BSX–DMF and BSX–DOX structures. The N...O distances involved are 2.951 (4) and 3.096 (4) Å compared with distances of 2.893 and 2.989 Å in BSX–DMF and 3.033 and 3.105 Å in BSX–DOX. Using the van der Waals radii of Pauling (1960) for N and O the above contacts do not appear unusual. However, contact distances are anisometric (Bondi, 1964; Nyburg & Faerman, 1985) and a contact distance of the order of 3.2 Å would be expected where π -bonding electrons are involved. In each of the three BSX–solvate structures, the BSX carbonyl O atoms in the dimer lie approximately on the normals to the nitramine planes through the nitro N atoms. The interactions resemble those occurring between carbonyl O atoms and carbonyl C atoms in the structures of alloxan (Bolton, 1964), tetrachloro-*p*-benzoquinone (Chu, Jeffrey & Sakurai, 1962; van Weperen & Visser, 1972), anhydrous barbituric acid (Bolton, 1963), parabanic acid (Davies, 1955), 1,2,3-indantrione (Bolton, 1965), urea-parabanic acid (Colman & Medlin, 1970) and 2,6-dichloro-*p*-benzoquinone (Rees, 1970). In these compounds short C...O contact distances varying between 2.77 and 2.90 Å replace the hydrogen bonds which otherwise might be expected to occur. A recent accurate determination of the charge density in alloxan (Swaminathan, Craven & McMullan, 1985) does not support an earlier view that these interactions are polar in nature. In the case of the present nitro compounds, however, the charge distribution usually assigned to the nitro group would make the positively charged nitro N an especially favoured site for the attraction of a carbonyl O.

Although these N...O distances are indicative of only weak interaction between the dimers, the packing geometry may be favourable on account of the 'bite' of two nitro N atoms on each carbonyl O. A similar 'bite' is made upon an O of a solvent molecule by a different pair of N atoms on the outside of the dimer. Strong evidence of the stability of the group comprising the dimer and two solvent molecules is that it persists, relatively unchanged, in the three types of complex studied. The similarity can be noted if Fig. 4 is

compared with the corresponding projections for the BSX-DMF and BSX-DOX structures (Cobbedick & Small, 1973*b,c*). The difference in the three types of structure lies in the symmetry of packing of the units (2 BSX + 2 solvent), the determining factor being the difference in solvent-molecule profile involved. In the present structure the closest contacts between BSX and solvent are $N(4) \cdots O(14)$, 3.035 Å and $N(6) \cdots O(14)$, 2.844 Å compared with 2.891 and 2.969 Å in BSX-DMF and 3.116 and 3.199 Å in BSX-DOX.

Although many nitramine-solvent complexes have been reported to exist, only three other structure determinations have been reported. In the complex of hexahydro-1,3,5-trinitro-1,3,5-triazine and tetrahydrothiophene 1,1-dioxide (sulfolane) contacts between N (nitro) and O (sulfolane) of 3.02 and 3.13 Å are found (Haller, Brill & Rheingold, 1984). In the structures of the complexes of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane with *N,N*-dimethylformamide (Cobbedick & Small, 1975) and *N*-methyl-2-pyrrolidinone (Haller, Rheingold & Brill, 1985) no short contacts between solvent molecules and the nitramine are reported. In both of these structures the solvent molecules are disordered. Disorder is not uncommon in structures involving small solvent molecules; no ready explanation is offered for the disorder in the present structure.

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Structure of 4-*tert*-Butyl-2,2,6,6-tetramethylcyclohexanol

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Abstract. $C_{14}H_{28}O$, $M_r = 212.38$, monoclinic, $P2_1/n$, $a = 6.047$ (1), $b = 17.224$ (2), $c = 26.708$ (5) Å, $\beta = 91.46$ (2)°, $V = 2780.8$ (8) Å³, $Z = 8$, $D_x =$

1.014 Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.06$ mm⁻¹, $F(000) = 952$, $T = 295$ K, $R = 0.076$ for 902 observed diffractometer data. The structure has

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