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The Crystallography of Nitramine–Solvent Complexes.
V.* The Crystal Structure of 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane

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The crystal structure of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) has been solved with counter data. The crystals are monoclinic, space group $C2/c$, with $a = 26.935$ (4), $b = 9.174$ (1) $c = 6.122$ (1) Å, $\beta = 101.35$ (3)°; $Z = 4$. Atomic positional and anisotropic thermal vibration parameters have been refined by the method of least squares to produce a final R of 0·115.

Introduction

The crystal structures of three solvates of BSX have been determined (Cobbledick & Small, 1973*a*, *b*, *c*) in which the interaction of the acetoxy C=O oxygen atom of one BSX molecule with two nitro nitrogen atoms of adjacent groups of a BSX molecule related by a centre of symmetry is a common feature. The crystal structure of BSX has been studied in order to give a comparison of the molecular shape and environment in the pure and complexed state.

Experimental

Although crystallization of BSX from acetone at 0 °C gives needle crystals of a 1:1 complex, crystallization at room temperature yields tabular crystals of pure BSX. Oscillation and Weissenberg photographs showed the plate-shaped crystals to be monoclinic. Absent spectra, hkl when $(h+k) = 2n+1$ and $h0l$ when $l = 2n+1$, indicated the space group to be either Cc or $C2/c$. The space group ($C2$ or Cm or $C2/m$) reported earlier (Claringbull & Small, 1971) has now been found to be incorrect and the dimensions given in that paper refer to a body-centred unit cell.

A least-squares fit of a number of θ values of reflexions measured on a three-circle diffractometer was used to determine cell dimensions. Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) was used for this and for the collection of intensities. Crystal data for BSX are given in Table 1.

Table 1. *Crystal data*

$a = 26.935$ (4) Å
$b = 9.174$ (1)
$c = 6.122$ (1)
$\beta = 101.35$ (3)°
$V = 1483.1$ Å^3
$Z = 4$
$D_o = 1.58$ g cm^{-3}
$D_c = 1.586$ g cm^{-3}

A single crystal of dimensions 0·8 × 0·8 × 0·3 mm was used for the collection of intensities on a three-circle diffractometer. Integrated intensities of 1645 unique reflexions in the copper sphere were measured up to a $\sin\theta/\lambda$ value of 0·642 Å^{-1}, of which 61 were non-observable ($I < 1\sigma$). The intensities were corrected for absorption with the program *ABSCOR* which is available on the X-RAY 63 System.

Determination and refinement of the structure

The distribution of the intensities was found to be centric by the $N(z)$ statistical test (Howells, Phillips & Rogers, 1950) and the space group on this evidence was assumed to be $C2/c$. With four molecules in the unit cell the BSX molecule must possess either a centre of symmetry or a twofold axis. A centrosymmetric BSX molecule can be ruled out and thus the BSX molecule has a crystallographic twofold axis along the central N–N bond. This is reasonable in view of the observation that for the three BSX solvate structures which have been determined, in which no symmetry restriction applies, the approach to twofold symmetry of the BSX molecule is quite evident.

The structure was solved by direct methods with the program *MULTAN* (Germain, Main & Woolfson, 1971). Four unique sets of phases for starting reflexions ($E > 1.5$) were produced and an E map calculated with the set of signs of highest figure of merit revealed 8 out of the 12 heavy atoms of the asymmetric unit. An $(F_o - F_c)$ map gave the positions of the 4 remaining atoms. Refinement was carried out by the method of least-squares with the full-matrix program *FMLS* (Bracher & Taylor, 1967). Refinement of the carbon, nitrogen and oxygen parameters continued until $R\ (= \sum|F_o| - |F_c|/\sum|F_o|)$ reached 0·128. An $(F_o - F_c)$ synthesis gave the positions of the 7 hydrogen atoms of the asymmetric unit and revealed peaks and ridges of electron density which could not be explained chemically or in terms of disorder. The hydrogen atoms were assigned isotropic temperature factors based on the anisotropic ones of the atoms to which they were bonded. Two cycles of refinement of the heavy atoms

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* Part IV: Cobbledick & Small (1973*b*).

and one cycle of refinement of the hydrogen positional coordinates gave a final R of 0·115. All reflexions were weighted equally and the scattering factors used were from *International Tables for X-ray Crystallography* (1962). Final coordinates are shown in Table 2 and the vibration parameters of the heavier atoms in Table 3. Values of the observed and calculated structure amplitudes are listed in Table 4. The poor agreement between observed and calculated structure factors and the residual electron densities on the $(F_o - F_c)$ map may be due to a breakdown of the crystal structure during the collection of intensities. Several months after the intensity measurements were completed, the crystal used was found to have become opaque, and gave rise to considerably broadened reflexions.

Table 2. *Fractional atomic coordinates*

The values of the fractional coordinates and the estimated standard deviations in parentheses are multiplied by 10^5.

	x	y	z
C(1)	18939 (23)	25142 (61)	63119 (91)
C(2)	13451 (27)	18011 (69)	29040 (121)
C(3)	4674 (21)	25244 (53)	34988 (76)
C(7)	21778 (26)	37604 (76)	73925 (99)
N(1)	8534 (16)	24068 (44)	21072 (65)
N(2)	8046 (19)	33447 (54)	2999 (74)
N(3)	0	17972 (55)	25000
N(4)	0	3167 (57)	25000
O(1)	16632 (17)	28538 (45)	41921 (66)
O(2)	11635 (18)	34547 (75)	− 6188 (78)
O(3)	3970 (16)	39456 (48)	− 2594 (67)
O(4)	3997 (16)	− 2971 (37)	32526 (54)
O(9)	18444 (26)	13257 (55)	70591 (85)
H(1)	13009 (286)	10204 (926)	38230 (1214)
H(2)	15451 (284)	12940 (863)	14535 (1265)
H(3)	6001 (233)	20577 (707)	48260 (995)
H(4)	3786 (226)	36831 (732)	36815 (975)
H(9)	24871 (280)	39465 (878)	68540 (1139)
H(10)	19343 (271)	48019 (839)	73309 (1163)
H(11)	22999 (265)	34633 (875)	87098 (1180)

Discussion of the crystal structure

(*a*) *Arrangement of the BSX molecules*

The short intermolecular approaches between carbonyl oxygen atoms and nitro nitrogen atoms which have been found in the BSX solvate structures giving BSX dimer units are not present in the pure BSX structure. The closest intermolecular distances between heavy atoms occur between atoms of nitro groups of molecules related principally by the c glide. Intermolecular distances less than 3·30 Å between heavy atoms and less than 2·70 Å between heavy atoms and hydrogen atoms are shown in Table 5. The O(3)···H(4) distance of 2·268 (67) Å is particularly short but the standard deviation is large and the C–H bond is long. The C(3)–H(4)···O(3) angle is 164° and the possibility

Table 3. *Thermal vibrational parameters*

The b_{ij} values and the estimated standard deviations (in parentheses) are multiplied by 10^5 The temperature factor equation has the form $\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	147 (13)	1098 (67)	2935 (164)	148 (45)	386 (66)	208 (170)
C(2)	145 (14)	1067 (74)	4084 (234)	89 (50)	75 (82)	−376 (214)
C(3)	125 (11)	919 (57)	2074 (131)	− 94 (38)	469 (58)	−307 (137)
C(7)	185 (14)	1721 (96)	2908 (180)	− 97 (58)	− 10 (74)	145 (212)
N(1)	98 (9)	946 (50)	2492 (119)	154 (32)	387 (47)	198 (123)
N(2)	126 (10)	1415 (67)	2814 (139)	0 (40)	403 (55)	727 (157)
N(3)	130 (13)	568 (57)	2324 (158)	0 (—)	613 (67)	0 (—)
N(4)	204 (15)	632 (60)	1043 (127)	0 (—)	441 (65)	0 (—)
O(1)	180 (9)	1211 (55)	3302 (131)	−154 (34)	−266 (51)	681 (137)
O(2)	159 (10)	3791 (133)	4164 (170)	−286 (58)	1018 (65)	1816 (243)
O(3)	153 (9)	1560 (62)	3563 (136)	−3 (35)	278 (51)	2370 (151)
O(4)	205 (9)	800 (42)	2083 (99)	215 (30)	293 (44)	311 (101)
O(9)	508 (18)	1289 (67)	3815 (171)	−110 (56)	− 19 (86)	1110 (175)

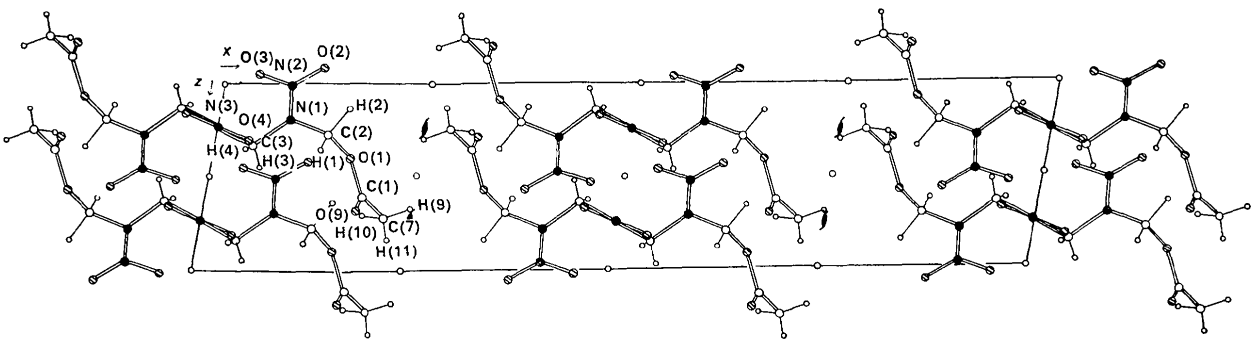

Fig. 1. The crystal structure projected on to (010).

of an intermolecular C–H···O hydrogen bond cannot be ruled out. Fig. 1 shows the structure projected on to (010) and the layered structure is consistent with the easy cleavage of crystals of BSX parallel to (100).

Table 4. *Observed and calculated structure amplitudes* × 10^2

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 5. *Intermolecular contacts* (Å)

$O(9)\cdots O(2^{i})$	3·198 (9)	$H(4)\cdots O(3^{v})$	2·27 (7)
$C(1)\cdots O(2^{i})$	3·098 (8)	$H(10)\cdots O(1^{v})$	2·60 (8)
$C(7)\cdots O(2^{i})$	3·215 (9)	$O(9)\cdots C(2^{vi})$	3·252 (9)
$O(3)\cdots O(3^{ii})$	2·947 (8)	$O(4)\cdots O(4^{vi})$	3·109 (7)
$N(4)\cdots N(4^{iii})$	3·116 (2)	$O(4)\cdots N(1^{vi})$	3·110 (5)
$N(4)\cdots O(4^{iii})$	3·004 (4)	$O(9)\cdots H(2^{vi})$	2·54 (8)
$O(3)\cdots O(3^{iv})$	3·129 (7)	$O(4)\cdots N(2^{vi})$	3·168 (6)

The superscripts indicate the equivalent positions as follows:

x	y	z	Superscript None
x	y	$1+z$	i
$-x$	$1-y$	$-z$	ii
$-x$	$-y$	$1-z$	iii
$-x$	y	$-\frac{1}{2}-z$	iv
x	$1-y$	$\frac{1}{2}+z$	v
x	$-y$	$\frac{1}{2}+z$	vi

(*b*) *Shape of the BSX molecule*

The BSX molecule has crystallographic twofold symmetry with the nitrogen atoms of the central N–N bond lying on a twofold axis. Bond lengths and angles are given in Tables 6 and 7 and are comparable with those of BSX in the solvate structures. The nitramine groups (C_2NNO_2) and the carboacetoxy groups ($C.O\ CO.CH_3$) are approximately planar and the deviations of atoms from the least-squares planes are listed in Table 8. The conformation of the BSX molecule can be defined in terms of the torsion angles along the C–N and C–O bonds which link these planar groups. Table 9 shows the four torsion angles defining the symmetric BSX molecule in the pure BSX structure in comparison with the eight angles defining the molecule in the *N*,*N*-dimethylformamide, 1,4-dioxane and 4-hydroxybutanoic acid lactone complex structures. The correspondence illustrates the extent to which the molecular shapes differ in the complexed and pure crystals; the only major difference between the molecules is a relative rotation of the acetyl groups of about 42° in pure BSX. The conformation of the molecule is illustrated in Fig. 2.

Table 6. *Bond distances and their standard deviations* (Å)

C(7)–C(1)	1·460 (9)	N(4)–O(4)	1·222 (5)
C(1)–O(9)	1·200 (8)	C(7)–H(9)	0·97 (8)
C(1)–O(1)	1·360 (6)	C(7)–H(10)	1·15 (8)
O(1)–C(2)	1·422 (8)	C(7)–H(11)	0·85 (7)
C(2)–N(1)	1·431 (8)	C(2)–H(1)	0·93 (8)
N(1)–N(2)	1·387 (6)	C(2)–H(2)	1·22 (8)
N(2)–O(2)	1·215 (8)	C(3)–H(3)	0·93 (6)
N(2)–O(3)	1·216 (6)	C(3)–H(4)	1·10 (7)
N(1)–C(3)	1·472 (7)		
C(3)–N(3)	1·449 (6)		
N(3)–N(4)	1·358 (7)		

There are a number of close intramolecular C–H···O contacts and the geometry of these contacts is shown in Table 10. The large deviations of the C–H···O angles from 180° suggest that the contacts represent minimum repulsion distances rather than C–H···O hydrogen bonds.

Table 7. *Bond angles and their standard deviations* (°)

C(7)–C(1)–O(9)	128·8 (5)	C(1)—C(7)–H(9)	113 (5)
C(7)–C(1)–O(1)	110·7 (5)	C(1)—C(7)–H(10)	113 (3)
O(9)–C(1)–O(1)	120·5 (5)	C(1)—C(7)–H(11)	104 (5)
C(1)–O(1)–C(2)	119·1 (5)	H(9)—C(7)–H(10)	111 (6)
O(1)–C(2)–N(1)	110·0 (5)	H(9)—C(7)–H(11)	100 (6)
C(2)–N(1)–C(3)	122·9 (5)	H(10)–C(7)–H(11)	114 (6)
C(2)–N(1)–N(2)	116·7 (5)	O(1)—C(2)–H(1)	109 (4)
N(2)–N(1)–C(3)	116·7 (4)	O(1)—C(2)–H(2)	111 (4)
N(1)–C(3)–N(3)	112·1 (3)	N(1)—C(2)–H(1)	107 (5)
N(1)–N(2)–O(2)	117·5 (5)	N(1)—C(2)–H(2)	114 (3)
N(1)–N(2)–O(3)	116·4 (5)	H(1)—C(2)–H(2)	106 (6)
O(2)–N(2)–O(3)	126·1 (5)	N(1)—C(3)–H(3)	106 (4)
C(3)–N(3)–C(3′)	125·2 (5)	N(1)—C(3)–H(4)	109 (3)
C(3)–N(3)–N(4)	117·4 (3)	N(3)—C(3)–H(3)	108 (4)
N(3)–N(4)–O(4)	117·4 (3)	N(3)—C(3)–H(4)	107 (3)
O(4)–N(4)–O(4′)	125·1 (5)	H(3)—C(3)–H(4)	114 (5)

Table 8. *Deviations of atoms from least-squares planes*

(*a*) Plane through atoms C(1), C(7), O(1) and O(9). Equation of the plane referred to orthogonal axes *a*, *b*, *c** is

$$-0{\cdot}8912x+0{\cdot}3126y+0{\cdot}3288z=-1{\cdot}8975$$

C(1)	−0·004 Å	O(9)	0·002 Å
C(7)	0·001	C(2)	0·070
O(1)	0·001		

(*b*) Plane through atoms N(1), N(2), O(2) and O(3). Equation of the plane referred to orthogonal axes *a*, *b*, *c** is

$$0{\cdot}2249x+0{\cdot}7615y+0{\cdot}6079z=2{\cdot}9135$$

N(1)	−0·003 Å	O(3)	−0·004 Å
N(2)	0·012	C(2)	0·140
O(2)	−0·004	C(3)	0·315

(*c*) Plane through atoms N(3), N(4), O(4) and O(4′). Equation of the plane referred to orthogonal axes *a*, *b*, *c** is

$$-0{\cdot}4165x+0{\cdot}0000y+0{\cdot}9091z=1{\cdot}4897$$

N(3)	0·000 Å	O(4′)	0·000 Å
N(4)	0·000	C(3)	0·071
O(4)	0·000	C(3′)	−0·071

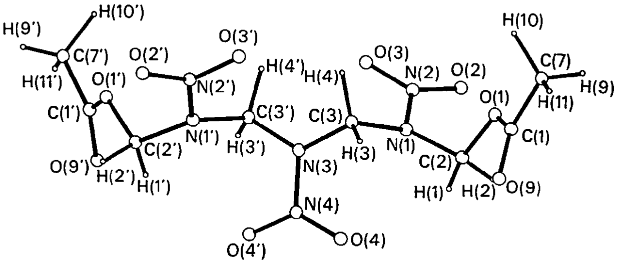

Fig. 2. The BSX molecule.

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Table 9. *Torsion angles for BSX and its complexes with N,N-dimethylformamide* (*BSX–DMF*), 1,4-*dioxane* (*BSX–DOX*) *and* 4-*hydroxybutanoic acid lactone* (*BSX–BL*)

	BSX	BSX-DMF	BSX-DOX	BSX-BL
C(1)–O(1)–C(2)–N(1)	+124·6°	+82·6°	−85·0°	+86·2°
O(1)–C(2)–N(1)–N(2)	+77·6	+78·4	−76·7	+78·0
N(2)–N(1)–C(2)–N(3)	+79·0	+67·9	−71·2	+70·3
N(1)–C(3)–N(3)–N(4)	+72·6	+71·8	−71·1	+73·3
N(4)–N(3)–C(4)–N(5)	—	+70·2	−75·6	+75·6
N(3)–C(4)–N(5)–N(6)	—	+74·8	−76·9	+78·5
N(6)–N(5)–C(5)–O(8)	—	+72·5	−76·2	+72·0
N(5)–C(5)–O(8)–C(6)	—	+80·0	−82·7	+85·6

Table 10. *Geometry of the intramolecular* C–H···O *contacts*

Distance (Å)		Angle (°)	
O(4)···C(2)	3·232 (8)	C(2) –H(1) ···O(4)	119
O(4)···H(1)	2·67 (8)	C(3′)–H(4′)···O(3)	110
O(3)···C(3′)	3·045 (7)	C(2) –H(1) ···O(9)	107
O(3)···H(4′)	2·48 (7)		
O(9)···C(2)	2·669 (8)		
O(9)···H(1)	2·24 (7)		

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