

the zwitterion is held in the active site of the enzyme by the carboxyl and $-\text{NH}_3^+$ groups then it is not possible to fit the cyclopentane derivative onto the crystallographically determined shapes for methionine. This may imply that the methionine molecule is not in an extended conformation in the active site of the enzyme (Lombardini *et al.*, 1970). Further studies of other inhibitors to the system are in progress.

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The Crystallography of Nitramine–Solvent Complexes. IV.* The Crystal Structure of the 1:1 Molecular Complex Formed by 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,4-Dioxane

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The crystal structure of the 1:1 molecular complex formed by 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,4-dioxane (BSX–DOX) has been solved by direct methods with counter measured X-ray data. The crystals are monoclinic, space group $P2_1/n$, with $a = 22.134$ (3), $b = 13.828$ (4), $c = 6.498$ (1) Å, $\beta = 96.72$ (6)° and $Z = 4$. Least-squares refinement gave a final R of 0.0600. A feature of the structure is the presence of dimers of BSX in which the carbonyl oxygen atom of one BSX molecule interacts with the nitrogen atoms of two adjacent nitro groups in a BSX molecule related by a centre of symmetry. The $\text{N} \cdots \text{O}$ distances are 3.033 and 3.105 Å. The dioxane molecules lie in channels between columns of BSX dimer units so that one oxygen atom of each molecule lies between two adjacent nitro groups. In this case the $\text{N} \cdots \text{O}$ distances are 3.116 and 3.199 Å.

Introduction

BSX is of interest because of the readiness with which it forms complexes with solvents. Usually simple re-

crystallization from the solvent will yield needles of the solvent complex. The complex crystals from different solvents may be divided into four groups (type A, B, C or D); within each group the cell dimensions are similar and the internal symmetry the same (Cobbledick & Small, 1973a). The crystal structure determina-

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tion of the 1:1 BSX-*N,N*-dimethylformamide complex (BSX-DMF) has already been reported (Cobbledick & Small, 1973*b*). It is of type *A* and in order to derive further information about these compounds this investigation of the crystal structure of the type *C* 1:1 complex formed between BSX and 1,4-dioxane (BSX-DOX) has been carried out.

Acicular crystals of BSX-DOX, elongated in the *b* direction, were grown by evaporation of solvent from a solution of BSX in excess 1,4-dioxane at room temperature. When removed from solution the crystals gradually lost solvent and became pseudomorphic. Crystals used in the X-ray examination were enclosed in Lindemann glass tubes. Weissenberg photographs showed them to be monoclinic and the systematic absences, *h*0*l* when (*h*+*l*)=2*n*+1 and 0*k*0 when *k*=2*n*+1, indicated the space group to be *P*2₁/*n*. Unit-cell dimensions were calculated from a least-squares fit to interplanar spacings measured on a three-circle diffractometer (Small & Travers, 1961) with Cu *K*α radiation (λ=1.5418 Å). The density measured by flotation in a mixture of carbon tetrachloride and chlorobenzene indicated a BSX to solvent molecular ratio of 1:1. Crystal data are shown in Table 1.

Table 1. *Crystal data*

<i>a</i> = 22.134 (3) Å
<i>b</i> = 13.828 (4)
<i>c</i> = 6.498 (1)
β = 96.72 (6)°
<i>V</i> = 1975.2 Å ³
<i>Z</i> = 4 molecules of BSX + 4 molecules of 1,4-dioxane
<i>D</i> _{obs} = 1.49 g cm ⁻³
<i>D</i> _{calc} = 1.49 g cm ⁻³

A single crystal of dimensions 1.0 × 0.6 × 0.6 mm was used for the collection of intensities on a three-circle diffractometer. 4398 independent integrated intensities (*I* > 1σ) were measured up to sin θ/λ = 0.642 Å⁻¹. No correction was applied for absorption.

Determination and refinement of the structure

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The program produced 16 sets of signs for the phases of 269 reflexions (*E* > 1.9) and the set of phases with the highest figures of merit was used in the computation of an *E* map. The map revealed most of the atoms of a recognizable BSX molecule (20 out of 24 atoms), but the molecule required a translation of 4.4 Å parallel to *a* to give a reasonable model. The positional coordinates of the 20 atoms which had been located were refined by least-squares calculations for two cycles of refinement and the remaining 10 atoms were found on an (*F*_o - *F*_c) map. A least-squares refinement of the positional coordinates and anisotropic temperature factors of the carbon, nitrogen and oxygen atoms was carried out with the full-matrix program *FMLS*

(Bracher & Taylor, 1967) adapted for the ICL 1909 computer. Convergence was achieved at an *R* of 0.100. All 22 hydrogen atoms were located in an (*F*_o - *F*_c) synthesis. The hydrogen atoms were included in the model with isotropic temperature factors which were not refined at this stage. For the last two cycles of least-squares refinement the hydrogen atom positions and their *B* values were refined. The final *R* was 0.060 with a maximum shift to error in the parameters of the heavy atoms of 0.4. Atomic scattering factors were taken from *International Tables for X-ray Crystal-*

Table 2. *Final fractional atomic coordinates*

The values of the fractional coordinates and the estimated standard deviations are multiplied by 10⁵.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-24184 (11)	22715 (19)	21454 (42)
C(2)	-21326 (12)	12645 (23)	50414 (43)
C(3)	-10280 (11)	18364 (17)	55674 (36)
C(4)	-296 (10)	13852 (16)	77707 (36)
C(5)	7565 (11)	22202 (19)	103755 (40)
C(6)	14155 (12)	8602 (19)	105683 (39)
C(7)	-28133 (12)	23327 (20)	1301 (41)
C(8)	20559 (12)	5495 (20)	106058 (43)
C(9)	8224 (14)	56321 (23)	- 2003 (50)
C(10)	14864 (14)	53888 (23)	3025 (48)
C(11)	6725 (14)	53414 (24)	32227 (55)
C(12)	13354 (14)	51149 (23)	37240 (49)
N(1)	-14920 (10)	10971 (15)	50955 (32)
N(2)	-12926 (12)	1899 (16)	46078 (36)
N(3)	- 6581 (8)	16958 (14)	75355 (28)
N(4)	- 9238 (10)	18512 (16)	92824 (32)
N(5)	3985 (9)	21514 (15)	83904 (33)
N(6)	5246 (10)	28080 (17)	68840 (37)
O(1)	-24306 (8)	13683 (13)	29663 (29)
O(2)	-16889 (12)	- 4306 (16)	42522 (38)
O(3)	- 7454 (10)	824 (15)	46256 (34)
O(4)	-14695 (8)	20354 (16)	90738 (30)
O(5)	- 5963 (9)	17922 (17)	109370 (28)
O(6)	2282 (9)	27251 (16)	51980 (31)
O(7)	9146 (10)	34132 (16)	73801 (38)
O(8)	13572 (8)	18289 (13)	103479 (30)
O(9)	-21280 (9)	29177 (14)	30052 (32)
O(10)	9861 (9)	3403 (15)	107434 (36)
O(11)	5804 (9)	60120 (15)	15686 (36)
O(12)	15742 (9)	47167 (15)	19616 (33)
H(1)	-21672 (122)	18824 (203)	58906 (417)
H(2)	-23015 (138)	5890 (228)	56012 (473)
H(3)	-12328 (117)	24014 (193)	55064 (394)
H(4)	- 7502 (118)	18360 (195)	44477 (400)
H(5)	243 (101)	8642 (166)	87341 (345)
H(6)	406 (101)	10918 (167)	64770 (347)
H(7)	8200 (131)	28548 (218)	109241 (444)
H(8)	5277 (117)	18233 (195)	112918 (398)
H(9)	-26564 (136)	27341 (234)	- 6027 (461)
H(10)	-31790 (141)	24457 (234)	2743 (478)
H(11)	-28460 (143)	17834 (246)	- 5948 (487)
H(12)	22005 (162)	8071 (275)	96633 (576)
H(13)	23195 (172)	7323 (291)	117457 (609)
H(14)	20463 (179)	- 1638 (311)	105294 (620)
H(15)	5378 (160)	50110 (277)	- 6155 (559)
H(16)	8065 (183)	60914 (310)	- 13236 (627)
H(17)	17448 (141)	60257 (235)	6873 (481)
H(18)	17136 (145)	50924 (247)	- 8282 (501)
H(19)	4940 (150)	56247 (250)	43535 (519)
H(20)	4098 (151)	47081 (252)	25591 (517)
H(21)	13524 (164)	45696 (274)	48165 (562)
H(22)	15843 (151)	57294 (254)	38667 (516)

Table 3. *Thermal parameters*(a) Anisotropic b_{ij} values for the C, N and O atomsThe b_{ij} values and the estimated standard deviations are multiplied by 10^5 . The temperature factor equation has the form

$$\exp \{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}.$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	172 (5)	441 (14)	2704 (73)	77 (14)	359 (31)	8 (52)
C(2)	194 (6)	731 (20)	2396 (71)	-113 (17)	99 (33)	575 (60)
C(3)	179 (5)	412 (13)	2003 (58)	9 (13)	216 (27)	24 (44)
C(4)	161 (5)	435 (12)	2380 (60)	80 (12)	224 (26)	3 (43)
C(5)	200 (5)	591 (16)	2789 (71)	44 (15)	98 (31)	-516 (54)
C(6)	210 (6)	484 (15)	2164 (64)	-15 (15)	-17 (31)	288 (49)
C(7)	210 (6)	623 (16)	2778 (71)	55 (16)	15 (32)	284 (55)
C(8)	202 (6)	655 (17)	3020 (76)	69 (16)	79 (33)	592 (59)
C(9)	291 (8)	729 (20)	3642 (96)	173 (20)	-169 (43)	-219 (71)
C(10)	279 (7)	766 (20)	3387 (90)	128 (20)	435 (41)	28 (69)
C(11)	265 (8)	719 (20)	4702 (114)	104 (20)	793 (48)	187 (78)
C(12)	285 (8)	684 (19)	3618 (92)	142 (20)	379 (43)	206 (68)
N(1)	205 (5)	422 (11)	2367 (55)	-19 (12)	79 (26)	-123 (40)
N(2)	369 (7)	435 (13)	2365 (62)	-17 (16)	-80 (34)	-223 (45)
N(3)	153 (4)	478 (11)	1702 (45)	18 (11)	346 (21)	-194 (37)
N(4)	197 (5)	588 (14)	2042 (54)	-65 (13)	492 (26)	-240 (43)
N(5)	169 (4)	484 (12)	2401 (56)	-1 (12)	216 (25)	156 (42)
N(6)	216 (5)	519 (13)	3109 (68)	25 (13)	571 (30)	247 (49)
O(1)	207 (4)	506 (11)	2667 (52)	-84 (11)	-64 (23)	217 (38)
O(2)	462 (8)	525 (13)	3954 (76)	-273 (17)	-397 (39)	-308 (51)
O(3)	330 (6)	601 (13)	3523 (66)	257 (14)	349 (32)	-778 (48)
O(4)	178 (4)	832 (15)	2895 (55)	22 (12)	564 (24)	-628 (46)
O(5)	255 (5)	979 (17)	1720 (45)	-75 (15)	248 (24)	-183 (44)
O(6)	287 (5)	789 (15)	2711 (56)	-63 (15)	380 (28)	638 (47)
O(7)	285 (6)	623 (14)	4647 (81)	-260 (14)	578 (34)	174 (54)
O(8)	183 (4)	476 (10)	3142 (56)	-40 (10)	-43 (23)	-40 (39)
O(9)	279 (5)	465 (11)	3328 (61)	1 (12)	109 (28)	-297 (41)
O(10)	221 (5)	599 (13)	4384 (75)	-92 (13)	88 (30)	964 (50)
O(11)	244 (5)	583 (13)	4408 (75)	182 (13)	311 (31)	-75 (50)
O(12)	258 (5)	639 (13)	3479 (64)	223 (13)	248 (29)	121 (47)

Table 3 (cont.)

(b) Isotropic B values for the H atoms, with estimated standard deviations

	B (\AA^2)
H(1)	1.828 (612)
H(2)	3.757 (738)
H(3)	1.888 (562)
H(4)	2.427 (577)
H(5)	1.216 (465)
H(6)	1.189 (469)
H(7)	3.491 (694)
H(8)	2.385 (583)
H(9)	4.182 (726)
H(10)	12.292 (785)
H(11)	4.342 (791)
H(12)	5.162 (926)
H(13)	7.239 (1039)
H(14)	7.319 (1103)
H(15)	6.247 (972)
H(16)	7.203 (1191)
H(17)	4.610 (780)
H(18)	5.026 (828)
H(19)	5.418 (866)
H(20)	6.537 (882)
H(21)	8.100 (999)
H(22)	4.064 (877)

lography (1962), and all observable reflexions were given unit weight. The final positional parameters are shown in Table 2, the thermal vibration parameters in

Table 3(a) and (b) and the observed and calculated structure amplitudes in Table 4.

Discussion of the crystal structure

(a) Arrangement of the BSX molecules

Pairs of BSX molecules, related by a centre of symmetry, approach so that the acetyl oxygen atom of one molecule lies approximately equidistant between two nitro nitrogen atoms of adjacent groups on the other molecule. Similar dimer units have been found in the BSX-DMF structure. The two N...O approach distances are N(4)...O(10) = 3.033 (3) and N(2)...O(10) = 3.105 (3) Å compared with the shorter distances of 2.893 and 2.989 Å in the BSX-DMF structure. Dimer units related by the c translation are packed to give continuous columns and the arrangement of columns leaves channels parallel to c in which the dioxane molecules are accommodated. The only other particularly short contact between BSX molecules is one of 2.35 (3) Å between atoms O(5) and H(4) of molecules in the columns related by the c translation. The C(3)H(4)...O(5) angle is 151° and by some criteria this could be an example of an intermolecular C-H...O hydrogen bond. A similar contact has been found in the BSX-DMF structure. There are intramolecular

Table 4. *Observed and calculated structure amplitudes* $\times 10^2$

hkl	Observed	Calculated
100	100	100
110	110	110
111	111	111
200	200	200
210	210	210
211	211	211
220	220	220
221	221	221
300	300	300
310	310	310
311	311	311
320	320	320
321	321	321
330	330	330
331	331	331
400	400	400
410	410	410
411	411	411
420	420	420
421	421	421
430	430	430
431	431	431
440	440	440
441	441	441
500	500	500
510	510	510
511	511	511
520	520	520
521	521	521
530	530	530
531	531	531
540	540	540
541	541	541
600	600	600
610	610	610
611	611	611
620	620	620
621	621	621
630	630	630
631	631	631
640	640	640
641	641	641
650	650	650
651	651	651
700	700	700
710	710	710
711	711	711
720	720	720
721	721	721
730	730	730
731	731	731
740	740	740
741	741	741
750	750	750
751	751	751
800	800	800
810	810	810
811	811	811
820	820	820
821	821	821
830	830	830
831	831	831
840	840	840
841	841	841
850	850	850
851	851	851
900	900	900
910	910	910
911	911	911
920	920	920
921	921	921
930	930	930
931	931	931
940	940	940
941	941	941
950	950	950
951	951	951
1000	1000	1000
1010	1010	1010
1011	1011	1011
1020	1020	1020
1021	1021	1021
1030	1030	1030
1031	1031	1031
1040	1040	1040
1041	1041	1041
1050	1050	1050
1051	1051	1051
1100	1100	1100
1110	1110	1110
1111	1111	1111
1120	1120	1120
1121	1121	1121
1130	1130	1130
1131	1131	1131
1140	1140	1140
1141	1141	1141
1150	1150	1150
1151	1151	1151
1200	1200	1200
1210	1210	1210
1211	1211	1211
1220	1220	1220
1221	1221	1221
1230	1230	1230
1231	1231	1231
1240	1240	1240
1241	1241	1241
1250	1250	1250
1251	1251	1251
1300	1300	1300
1310	1310	1310
1311	1311	1311
1320	1320	1320
1321	1321	1321
1330	1330	1330
1331	1331	1331
1340	1340	1340
1341	1341	1341
1350	1350	1350
1351	1351	1351
1400	1400	1400
1410	1410	1410
1411	1411	1411
1420	1420	1420
1421	1421	1421
1430	1430	1430
1431	1431	1431
1440	1440	1440
1441	1441	1441
1450	1450	1450
1451	1451	1451
1500	1500	1500
1510	1510	1510
1511	1511	1511
1520	1520	1520
1521	1521	1521
1530	1530	1530
1531	1531	1531
1540	1540	1540
1541	1541	1541
1550	1550	1550
1551	1551	1551
1600	1600	1600
1610	1610	1610
1611	1611	1611
1620	1620	1620
1621	1621	1621
1630	1630	1630
1631	1631	1631
1640	1640	1640
1641	1641	1641
1650	1650	1650
1651	1651	1651
1700	1700	1700
1710	1710	1710
1711	1711	1711
1720	1720	1720
1721	1721	1721
1730	1730	1730
1731	1731	1731
1740	1740	1740
1741	1741	1741
1750	1750	1750
1751	1751	1751
1800	1800	1800
1810	1810	1810
1811	1811	1811
1820	1820	1820
1821	1821	1821
1830	1830	1830
1831	1831	1831
1840	1840	1840
1841	1841	1841
1850	1850	1850
1851	1851	1851
1900	1900	1900
1910	1910	1910
1911	1911	1911
1920	1920	1920
1921	1921	1921
1930	1930	1930
1931	1931	1931
1940	1940	1940
1941	1941	1941
1950	1950	1950
1951	1951	1951
2000	2000	2000
2010	2010	2010
2011	2011	2011
2020	2020	2020
2021	2021	2021
2030	2030	2030
2031	2031	2031
2040	2040	2040
2041	2041	2041
2050	2050	2050
2051	2051	2051
2100	2100	2100
2110	2110	2110
2111	2111	2111
2120	2120	2120
2121	2121	2121
2130	2130	2130
2131	2131	2131
2140	2140	2140
2141	2141	2141
2150	2150	2150
2151	2151	2151
2200	2200	2200
2210	2210	2210
2211	2211	2211
2220	2220	2220
2221	2221	2221
2230	2230	2230
2231	2231	2231
2240	2240	2240
2241	2241	2241
2250	2250	2250
2251	2251	2251
2300	2300	2300
2310	2310	2310
2311	2311	2311
2320	2320	2320
2321	2321	2321
2330	2330	2330
2331	2331	2331
2340	2340	2340
2341	2341	2341
2350	2350	2350
2351	2351	2351
2400	2400	2400
2410	2410	2410
2411	2411	2411
2420	2420	2420
2421	2421	2421
2430	2430	2430
2431	2431	2431
2440	2440	2440
2441	2441	2441
2450	2450	2450
2451	2451	2451
2500	2500	2500
2510	2510	2510
2511	2511	2511
2520	2520	2520
2521	2521	2521
2530	2530	2530
2531	2531	2531
2540	2540	2540
2541	2541	2541
2550	2550	2550
2551	2551	2551
2600	2600	2600
2610	2610	2610
2611	2611	2611
2620	2620	2620
2621	2621	2621
2630	2630	2630
2631	2631	2631
2640	2640	2640
2641	2641	2641
2650	2650	2650
2651	2651	2651
2700	2700	2700
2710	2710	2710
2711	2711	2711
2720	2720	2720
2721	2721	2721
2730	2730	2730
2731	2731	2731
2740	2740	2740
2741	2741	2741
2750	2750	2750
2751	2751	2751
2800	2800	2800
2810	2810	2810
2811	2811	2811
2820	2820	2820
2821	2821	2821
2830	2830	2830
2831	2831	2831
2840	2840	2840
2841	2841	2841
2850	2850	2850
2851	2851	2851
2900	2900	2900
2910	2910	2910
2911	2911	2911
2920	2920	2920
2921	2921	2921
2930	2930	2930
2931	2931	2931
2940	2940	2940
2941	2941	2941
2950	2950	2950
2951	2951	2951
3000	3000	3000
3010	3010	3010
3011	3011	3011
3020	3020	3020
3021	3021	3021
3030	3030	3030
3031	3031	3031
3040	3040	3040
3041	3041	3041
3050	3050	3050
3051	3051	3051
3100	3100	3100
3110	3110	3110
3111	3111	3111
3120	3120	3120
3121	3121	3121
3130	3130	3130
3131	3131	3131
3140	3140	3140
3141	3141	3141
3150	3150	3150
3151	3151	3151
3200	3200	3200
3210	3210	3210
3211	3211	3211
3220	3220	3220
3221	3221	3221
3230	3230	3230
3231	3231	3231
3240	3240	3240
3241	3241	3241
3250	3250	3250
3251	3251	3251
3300	3300	3300
3310	3310	3310
3311	3311	3311
3320	3320	3320
3321	3321	3321
3330	3330	3330
3331	3331	3331
3340	3340	3340
3341	3341	3341
3350	3350	3350
3351	3351	3351
3400	3400	3400
3410	3410	3410
3411	3411	3411
3420	3420	3420
3421	3421	3421
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3431	3431	3431
3440	3440	3440
3441	3441	3441
3450	3450	3450
3451	3451	3451
3500	3500	3500
3510	3510	3510
3511	3511	3511
3520	3520	3520
3521	3521	3521
3530	3530	3530
3531	3531	3531
3540	3540	3540
3541	3541	3541
3550	3550	3550
3551	3551	3551
3600	3600	3600
3610	3610	3610
3611	3611	3611
3620	3620	3620
3621	3621	3621
3630	3630	3630
3631	3631	3631
3640	3640	3640
3641	3641	3641
3650	3650	3650
3651	3651	3651
3700	3700	3700
3710	3710	3710
3711	3711	3711
3720	3720	3720
3721	3721	3721
3730	3730	3730
3731	3731	3731
3740	3740	3740
3741	3741	3741
3750	3750	3750
3751	3751	3751
3800	3800	3800
3810	3810	3810
3811		

Table 4 (cont.)

Atom	x	y	z	Occupancy
N(1)	0.111	0.111	0.111	1.00
N(2)	0.222	0.222	0.222	1.00
N(3)	0.333	0.333	0.333	1.00
N(4)	0.444	0.444	0.444	1.00
N(5)	0.555	0.555	0.555	1.00
N(6)	0.666	0.666	0.666	1.00
O(1)	0.111	0.111	0.111	1.00
O(2)	0.222	0.222	0.222	1.00
O(3)	0.333	0.333	0.333	1.00
O(4)	0.444	0.444	0.444	1.00
O(5)	0.555	0.555	0.555	1.00
O(6)	0.666	0.666	0.666	1.00
O(7)	0.777	0.777	0.777	1.00
O(8)	0.888	0.888	0.888	1.00
O(9)	0.999	0.999	0.999	1.00
O(10)	0.111	0.111	0.111	1.00
O(11)	0.222	0.222	0.222	1.00
O(12)	0.333	0.333	0.333	1.00
C(1)	0.111	0.111	0.111	1.00
C(2)	0.222	0.222	0.222	1.00
C(3)	0.333	0.333	0.333	1.00
C(4)	0.444	0.444	0.444	1.00
C(5)	0.555	0.555	0.555	1.00
C(6)	0.666	0.666	0.666	1.00
C(7)	0.777	0.777	0.777	1.00
C(8)	0.888	0.888	0.888	1.00
C(9)	0.999	0.999	0.999	1.00
C(10)	0.111	0.111	0.111	1.00
C(11)	0.222	0.222	0.222	1.00
C(12)	0.333	0.333	0.333	1.00
C(13)	0.444	0.444	0.444	1.00
C(14)	0.555	0.555	0.555	1.00
C(15)	0.666	0.666	0.666	1.00
C(16)	0.777	0.777	0.777	1.00
C(17)	0.888	0.888	0.888	1.00
C(18)	0.999	0.999	0.999	1.00
C(19)	0.111	0.111	0.111	1.00
C(20)	0.222	0.222	0.222	1.00
C(21)	0.333	0.333	0.333	1.00
C(22)	0.444	0.444	0.444	1.00
H(1)	0.111	0.111	0.111	1.00
H(2)	0.222	0.222	0.222	1.00
H(3)	0.333	0.333	0.333	1.00
H(4)	0.444	0.444	0.444	1.00
H(5)	0.555	0.555	0.555	1.00
H(6)	0.666	0.666	0.666	1.00
H(7)	0.777	0.777	0.777	1.00
H(8)	0.888	0.888	0.888	1.00
H(9)	0.999	0.999	0.999	1.00
H(10)	0.111	0.111	0.111	1.00
H(11)	0.222	0.222	0.222	1.00
H(12)	0.333	0.333	0.333	1.00
H(13)	0.444	0.444	0.444	1.00
H(14)	0.555	0.555	0.555	1.00
H(15)	0.666	0.666	0.666	1.00
H(16)	0.777	0.777	0.777	1.00
H(17)	0.888	0.888	0.888	1.00
H(18)	0.999	0.999	0.999	1.00
H(19)	0.111	0.111	0.111	1.00
H(20)	0.222	0.222	0.222	1.00
H(21)	0.333	0.333	0.333	1.00
H(22)	0.444	0.444	0.444	1.00

contacts between nitro oxygen atoms and methylene hydrogen atoms in the BSX molecule and these are described in a later section. Fig. 1 shows the structure projected down *c*.

(b) Arrangement of the dioxane molecules

The dioxane molecules are situated in channels between columns of BSX dimers and the arrangement is such that one of the oxygen atoms of each dioxane molecule is also almost equidistant from two nitro nitrogen atoms of adjacent groups of a BSX molecule. A similar solvent interaction has been found, involving the DMF oxygen atom, in the BSX-DMF structure. The $N \cdots O$ contact distances are $N(4) \cdots O(11) = 3.116$ (3) and $N(6) \cdots O(11) = 3.199$ (3) Å compared with 2.891 and 2.969 Å for BSX-DMF. These nitrogen-oxygen contacts are much longer than, but otherwise similarly disposed to, those found in the complex between 1,4-dioxane and dinitrogen tetroxide (Groth & Hassel, 1965) where the nitrogen atoms act as acceptors, the donors being the dioxane oxygen atoms and the $N \cdots O$ distance is 2.76 Å.

The lone pairs of the dioxane oxygen atom do not appear to be involved in the interaction with the BSX nitro nitrogen atoms. The nitrogen atoms $N(4)$ and $N(6)$ involved in the contact lie 1.27 and 1.31 Å respectively from the plane in which the oxygen lone pairs would be expected and the two $C-O \cdots N$ angles for each contact are $C(9)-O(11) \cdots N(4) = 98.2^\circ$, $C(11)-$

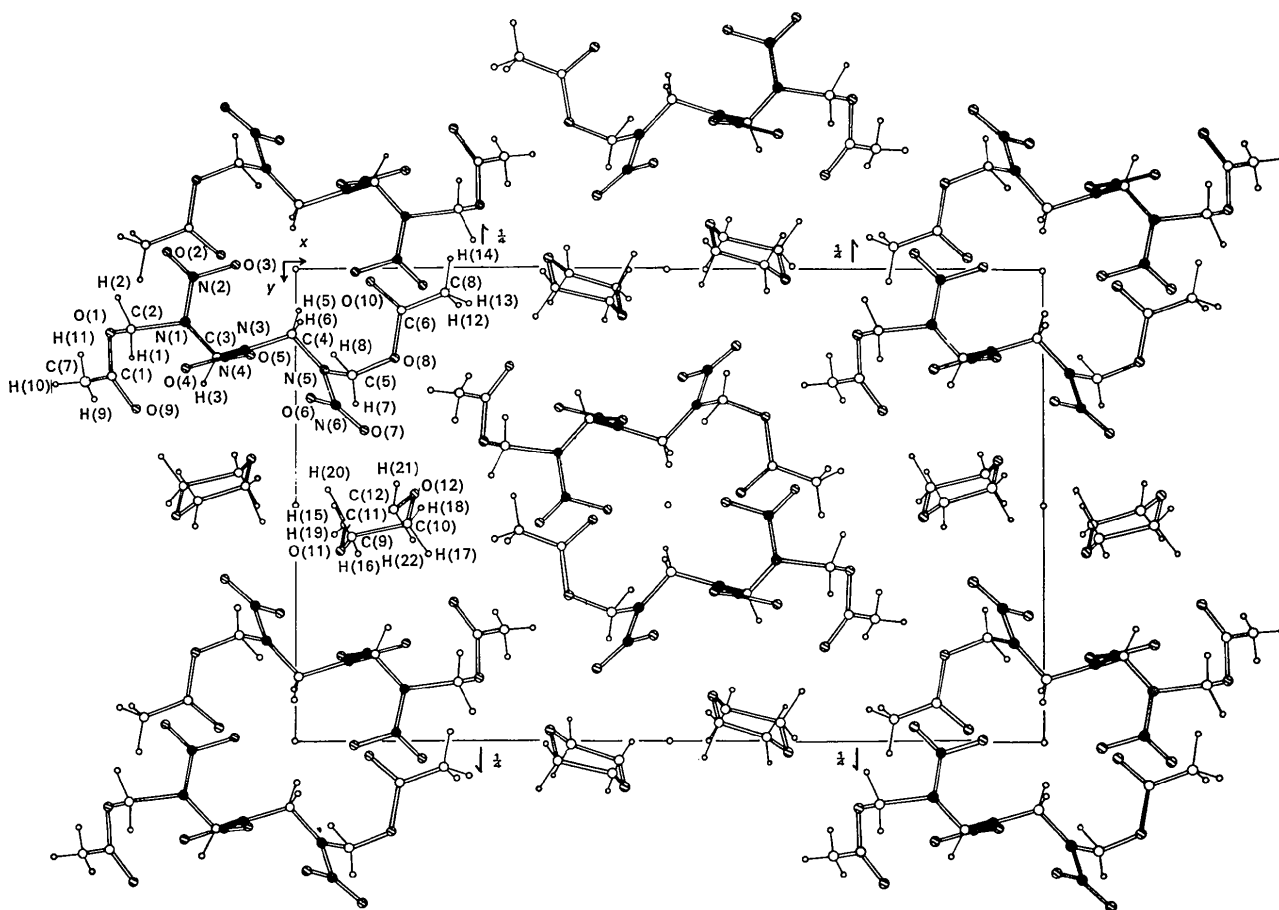


Fig. 1. The crystal structure projected down *c*.

O(11)···N(4)=137.6° and C(9)-O(11)···N(6)=150.8° and C(11)-O(11)···N(6)=98.2°.

(c) *Shape of the BSX molecule*

Bond distances and angles for the BSX molecule are given in Tables 5 and 6 respectively. An analysis of the anisotropic thermal motion with the program *MGTLS* of Gantzel & Trueblood indicated that the molecule as a whole was not librating as a rigid body and no correction was applied to the coordinates for libration. The molecule has approximate twofold symmetry

Table 5. *Bond distances and their standard deviations for the BSX molecule*

C(7)-C(1)	1.489 (4) Å	C(5)-O(8)	1.438 (3) Å
C(1)-O(9)	1.200 (3)	O(8)-C(6)	1.351 (3)
C(1)-O(1)	1.360 (3)	C(6)-O(10)	1.201 (3)
O(1)-C(2)	1.437 (3)	C(6)-C(8)	1.487 (4)
C(2)-N(1)	1.433 (3)	C(7)-H(9)	0.83 (3)
N(1)-N(2)	1.379 (3)	C(7)-H(10)	0.84 (3)
N(2)-O(2)	1.229 (3)	C(7)-H(11)	0.89 (3)
N(2)-O(3)	1.219 (3)	C(2)-H(1)	1.02 (3)
N(1)-C(3)	1.456 (3)	C(2)-H(2)	1.08 (3)
C(3)-N(3)	1.449 (3)	C(3)-H(3)	0.90 (3)
N(3)-N(4)	1.355 (3)	C(3)-H(4)	1.01 (3)
N(4)-O(4)	1.226 (3)	C(4)-H(5)	0.95 (2)
N(4)-O(5)	1.227 (3)	C(4)-H(6)	0.96 (2)
N(3)-C(4)	1.447 (3)	C(5)-H(7)	0.95 (3)
C(4)-N(5)	1.447 (3)	C(5)-H(8)	0.99 (3)
N(5)-N(6)	1.387 (3)	C(8)-H(12)	0.81 (4)
N(6)-O(6)	1.215 (3)	C(8)-H(13)	0.92 (4)
N(6)-O(7)	1.218 (3)	C(8)-H(14)	0.99 (4)
N(5)-C(5)	1.436 (3)		

about the central N-N bond. Within the molecule there are several short C-H···O contacts in which the H···O distances range from 2.33 to 2.51 Å. The geometries of these contacts are shown in Table 7. The C-H···O angles lie in the range 94–129°. Donohue (1968) has reviewed the evidence for C-H···O bonds and comes to the conclusion that they do not exist.

Table 7. *Geometry of intramolecular C-H···O contacts*

Distances (Å)		Angles (°)	
C(2)···O(9)	2.642 (4)	C(2)-H(1)···O(9)	94
H(1)···O(9)	2.37 (3)	C(3)-H(3)···O(9)	129
C(3)···O(9)	3.160 (3)	C(4)-H(6)···O(3)	120
H(3)···O(9)	2.51 (3)	C(2)-H(1)···O(4)	117
C(4)···O(3)	3.029 (3)	C(5)-H(8)···O(5)	122
H(6)···O(3)	2.44 (2)	C(3)-H(4)···O(6)	117
C(2)···O(4)	3.042 (3)	C(4)-H(5)···O(10)	127
H(1)···O(4)	2.44 (3)	C(5)-H(8)···O(10)	98
C(5)···O(5)	3.115 (3)		
H(8)···O(5)	2.47 (3)		
C(3)···O(6)	3.075 (3)		
H(4)···O(6)	2.49 (3)		
C(4)···O(10)	3.140 (3)		
H(5)···O(10)	2.47 (2)		
C(5)···O(10)	2.654 (3)		
H(8)···O(10)	2.33 (3)		

The three nitramine groups (C₂NNO₂) and the two end carboacetoxy groups (C.O.COCH₃) in the molecule are almost planar and the deviations of the atoms from the least-squares planes through these groups are

Table 6. *Bond angles and their standard deviations for the BSX molecule*

C(7)-C(1)-O(9)	126.5 (3)°	C(1)-C(7)-H(9)	107 (2)°
C(7)-C(1)-O(1)	111.1 (2)	C(1)-C(7)-H(10)	113 (2)
O(9)-C(1)-O(1)	122.4 (2)	C(1)-C(7)-H(11)	115 (2)
C(1)-O(1)-C(2)	115.6 (2)	H(9)-C(7)-H(10)	114 (3)
O(1)-C(2)-N(1)	112.5 (2)	H(9)-C(7)-H(11)	106 (3)
C(2)-N(1)-C(3)	124.3 (2)	H(10)-C(7)-H(11)	101 (3)
C(2)-N(1)-N(2)	118.9 (2)	O(1)-C(2)-H(1)	112 (2)
N(2)-N(1)-C(3)	116.8 (2)	O(1)-C(2)-H(2)	105 (2)
N(1)-C(3)-N(3)	113.8 (2)	N(1)-C(2)-H(1)	105 (2)
N(1)-N(2)-O(2)	115.9 (3)	N(1)-C(2)-H(2)	103 (2)
N(1)-N(2)-O(3)	116.9 (2)	H(1)-C(2)-H(2)	119 (2)
O(2)-N(2)-O(3)	127.1 (2)	N(1)-C(3)-H(3)	105 (2)
C(3)-N(3)-C(4)	124.8 (2)	N(1)-C(3)-H(4)	109 (2)
N(4)-N(3)-C(4)	117.7 (2)	N(3)-C(3)-H(3)	113 (2)
C(3)-N(3)-N(4)	117.5 (2)	N(3)-C(3)-H(4)	108 (1)
N(3)-C(4)-N(5)	113.7 (2)	H(3)-C(3)-H(4)	108 (2)
N(3)-N(4)-O(4)	117.3 (2)	N(3)-C(4)-H(5)	110 (1)
N(3)-N(4)-O(5)	117.0 (2)	N(3)-C(4)-H(6)	107 (1)
O(4)-N(4)-O(5)	125.7 (2)	N(5)-C(4)-H(5)	110 (1)
C(4)-N(5)-C(5)	125.0 (2)	N(5)-C(4)-H(6)	113 (1)
C(4)-N(5)-N(6)	117.5 (2)	H(5)-C(4)-H(6)	104 (2)
N(6)-N(5)-C(5)	117.1 (2)	N(5)-C(5)-H(7)	116 (2)
N(5)-C(5)-O(8)	112.2 (2)	N(5)-C(5)-H(8)	104 (1)
N(5)-N(6)-O(6)	116.3 (2)	O(8)-C(5)-H(7)	105 (2)
N(5)-N(6)-O(7)	117.2 (2)	O(8)-C(5)-H(8)	110 (2)
O(6)-N(6)-O(7)	126.5 (3)	H(7)-C(5)-H(8)	110 (2)
C(5)-O(8)-C(6)	116.3 (2)	C(6)-C(8)-H(12)	109 (3)
O(8)-C(6)-O(10)	122.9 (2)	C(6)-C(8)-H(13)	117 (3)
O(8)-C(6)-C(8)	111.2 (2)	C(6)-C(8)-H(14)	106 (2)
O(10)-C(6)-C(8)	125.9 (3)	H(12)-C(8)-H(13)	103 (4)
		H(12)-C(8)-H(14)	114 (4)
		H(13)-C(8)-H(14)	109 (3)

listed in Table 8. The shape of the molecule and the atom labelling is illustrated in Fig. 2.

Table 8. Deviations of atoms from least-squares planes (Å)

(a) Plane through atoms C(1), C(7), O(1) and O(9). Equation of the plane referred to orthogonal axes a, b, c^* $-0.8408x + 0.2564y + 0.4769z = 6.1089$			
C(1)	-0.006	O(9)	0.002
C(7)	0.002	C(2)	0.182
O(1)	0.002		
(b) Plane through atoms C(6), C(8), O(8) and O(10). Equation of the plane referred to orthogonal axes a, b, c^* $0.0230x + 0.1134y + 0.9933z = 6.9688$			
C(6)	-0.006	O(10)	0.003
C(8)	0.002	C(5)	0.050
O(8)	0.002		
(c) Plane through atoms N(1), N(2), O(2) and O(3). Equation of the plane referred to orthogonal axes a, b, c^* $-0.0290x - 0.2449y + 0.9691z = 2.9198$			
N(1)	0.003	O(3)	0.003
N(2)	-0.009	C(2)	-0.047
O(2)	0.003	C(3)	0.019
(d) Plane through atoms N(3), N(4), O(4) and O(5). Equation of the plane referred to orthogonal axes a, b, c^* $-0.2149x - 0.9755y + 0.0473z = -1.6213$			
N(3)	0.000	O(5)	0.000
N(4)	-0.001	C(3)	-0.106
O(4)	0.000	C(4)	0.131
(e) Plane through atoms N(5), N(6), O(6) and O(7). Equation of the plane referred to orthogonal axes a, b, c^* $-0.7321x + 0.6184y + 0.2857z = 3.2071$			
N(5)	0.001	O(7)	0.001
N(6)	-0.003	C(4)	-0.109
O(6)	0.001	C(5)	-0.044
(f) Plane through atoms C(9), C(10), C(11) and C(12). Equation of the plane referred to orthogonal axes a, b, c^* $0.1696x + 0.9617y + 0.2155z = 7.7675$			
C(9)	0.005	C(12)	0.005
C(10)	-0.005	O(11)	0.643
C(11)	-0.005	O(12)	-0.657

(d) The dioxane molecule

The dioxane molecules are in the preferred chair conformation (Fig. 1). The equation of the least-squares plane through the carbon atoms, referred to orthogonal axes a, b, c^* , and the deviations of atoms are shown in Table 8.

Thermal vibration of the molecule was analysed in terms of rotational oscillations of the molecule as a rigid body. For a molecule at a centrosymmetric site this motion can be described in terms of two tensors **T** and **L** but in other cases correlation of the librational and translation motion can occur. Schomaker & Trueblood (1968) have considered this correlation by the introduction of a third tensor, **S**. The tensors **T**, **L** and **S** were calculated from the b_{ij} values of the final cycle of least-squares refinement with the program *MGTLS* of Gantzel & Trueblood. Values of the rigid-body parameters referred to orthogonal axes a, b, c^* are given in Table 9. The satisfactory agreement obtained between U_{ij} values calculated from the **T**, **L** and **S** tensors and 'observed' U_{ij} values calculated from the b_{ij} values (Table 10) showed the reasonableness of the rigid-body description of the vibration.

Table 9. Rigid-body thermal parameters

Principal axes of L			
R.m.s. amplitude	Direction cosines ($\times 10^3$)		
7.7 ($^\circ$)	693	-681	238
6.2	268	-61	-961
4.6	669	730	140
Principal axes of reduced T			
R.m.s. amplitude	Direction cosines ($\times 10^3$)		
0.26 (Å)	-6	116	-994
0.23	-912	-408	-42
0.21	-411	905	108
Symmetrized screw tensor	$\begin{pmatrix} -153 & 262 & 68 \\ & 150 & -204 \\ & & 2 \end{pmatrix} \times 10^{-5} \text{ rad.}\text{Å}$		

The r.m.s. ΔU_{ij} value is 0.0016 Å² compared with a mean σU_{ij} of 0.0017 Å² calculated from the estimated standard deviation of the b_{ij} values. The atomic co-

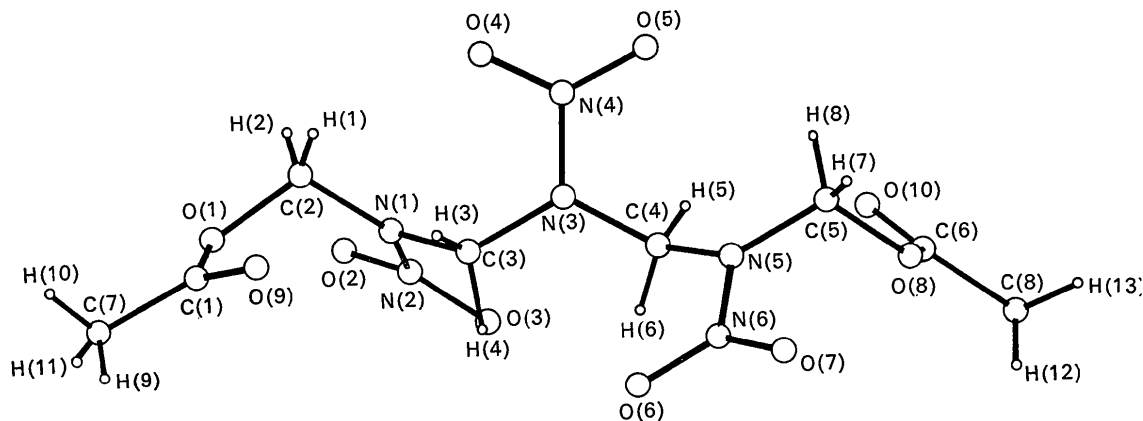


Fig. 2. The BSX molecule.

Table 10. *Observed and calculated values of ($U_{ij} \times 10^4$) in \AA^2*

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
C(9)	747	744	706	691	768	776	140	146	-152	-129	-49	-49
C(10)	665	653	742	741	715	709	98	117	73	61	6	22
C(11)	604	604	696	678	992	993	76	68	170	164	42	63
C(12)	686	687	663	670	763	711	105	111	47	52	47	45
O(11)	592	607	565	590	930	942	143	131	3	-20	-17	-25
O(12)	629	627	619	621	734	770	170	158	3	17	27	0

ordinates were corrected for libration and uncorrected and corrected bond lengths and angles for the molecule are given in Tables 11 and 12.

Table 11. *Bond distances and their standard deviations for the dioxane molecule*

	Before libration correction	After libration correction
C(9)—C(10)	1.506 (5) \AA	1.520 \AA
C(10)—O(12)	1.419 (4)	1.433
O(12)—C(12)	1.427 (4)	1.442
C(12)—C(11)	1.498 (4)	1.513
C(11)—O(11)	1.416 (4)	1.429
O(11)—C(9)	1.424 (4)	1.439
C(9)—H(15)	1.08 (4)	
C(9)—H(16)	0.96 (4)	
C(10)—H(17)	1.06 (3)	
C(10)—H(18)	1.02 (3)	
C(11)—H(19)	0.96 (3)	
C(11)—H(20)	1.11 (3)	
C(12)—H(21)	1.03 (4)	
C(12)—H(22)	1.01 (4)	

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Table 12. *Bond angles and their standard deviations for the dioxane molecule*

	Before libration correction	After libration correction
C(9)—C(10)—O(12)	110.8 (3)°	110.6°
C(10)—O(12)—C(12)	109.0 (2)	109.2
O(12)—C(12)—C(11)	110.6 (3)	110.5
C(12)—C(11)—O(11)	110.6 (3)	110.5
C(11)—O(11)—C(9)	109.7 (3)	109.8
O(11)—C(9)—C(10)	110.9 (3)	110.8
O(11)—C(9)—H(15)	103 (2)	
O(11)—C(9)—H(16)	113 (2)	
C(10)—C(9)—H(15)	114 (2)	
C(10)—C(9)—H(16)	105 (2)	
H(15)—C(9)—H(16)	111 (3)	
C(9)—C(10)—H(17)	111 (2)	
C(9)—C(10)—H(18)	119 (2)	
O(12)—C(10)—H(17)	110 (2)	
O(12)—C(10)—H(18)	104 (2)	
H(17)—C(10)—H(18)	102 (3)	
O(11)—C(11)—H(19)	106 (2)	
O(11)—C(11)—H(20)	102 (2)	
C(12)—C(11)—H(19)	114 (2)	
C(12)—C(11)—H(20)	112 (2)	
H(19)—C(11)—H(20)	112 (3)	
C(11)—C(12)—H(21)	105 (2)	
C(11)—C(12)—H(22)	111 (2)	
O(12)—C(12)—H(21)	106 (2)	
O(12)—C(12)—H(22)	99 (2)	
H(21)—C(12)—H(22)	125 (3)	

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