

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

BY R. E. COBBLEDICK AND R. W. H. SMALL

Chemistry Department, The University, Lancaster, England

(Received 21 March 1973; accepted 22 March 1973)

The crystal structure of the 1:1 molecular complex formed by 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and *N,N*-dimethylformamide (BSX–DMF) has been determined from three-dimensional X-ray diffraction data. Positional and anisotropic thermal vibrational parameters have been refined by least-squares methods giving a final *R* of 0.066. The crystals are monoclinic, space group $P2_1/n$ with $a = 15.359$ (3), $b = 19.789$ (4), $c = 6.412$ (2) Å, $\beta = 97.22$ (5)° and $Z = 4$. The structure consists of parallel columns of BSX dimers and channels in which the DMF molecules fit. The complex does not appear to be of the clathrate type; there are close contacts 2.893 and 2.989 Å between nitrogens of adjacent nitro groups of one BSX molecule and a carbonyl oxygen of its centrosymmetric pair. Similar approaches, 2.891 and 2.969 Å, also occur between adjacent nitro nitrogens and the DMF carbonyl oxygen atoms.

Introduction

Pure BSX crystallizes as plate-shaped crystals and the ability of BSX to yield needle-shaped crystals from certain organic solvents has been reported (Claringbull & Small, 1971; Cobbledick & Small, 1973*a*). These crystals lose solvent on standing and become opaque pseudomorphs. A large number of complexes with a wide variety of organic solvents has been prepared and these can be divided into four main types. Part II of this series of papers (Cobbledick & Small, 1973*a*) classified the various complexes into type *A*, *B*, *C* or *D*; within each group the cell dimensions are similar and the internal symmetry the same. The BSX–DMF complex is of type *A*, the commonest type encountered.

No structure determination of BSX or of its solvent complexes has been described in the literature and it was of interest to discover whether these compounds are clathrate in character or whether there are specific interactions or hydrogen bonding between the solvent and BSX molecules.

Experimental

Needle crystals of the BSX–DMF complex were grown by evaporation of a saturated solution of BSX in DMF at room temperature. The crystals lose solvent and become opaque in air and, for X-ray examination, crystals were sealed in Lindemann-glass capillary tubes. Oscillation and Weissenberg photographs showed the crystals to be monoclinic, and systematically absent reflexions $h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$ indicated the space group to be $P2_1/n$. Cell dimensions were determined by a least-squares fit of a number of θ values of reflexions measured on a three-circle diffractometer (Small & Travers, 1961) using

Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Measurement of the crystal density established a 1:1 molecular ratio of BSX to solvent and this was confirmed by thermogravimetric analysis and an n.m.r. spectrum of crystals dissolved in deuterated acetone. Crystal data for the complex are shown in Table 1.

Table 1. *Crystal data*

a	=	15.359 (3) Å
b	=	19.789 (4)
c	=	6.412 (2)
β	=	97.22 (5)°
V	=	1933.1 Å ³
Z	=	4 molecules of BSX + 4 molecules of DMF
D_{obs}	=	1.47 g cm ⁻³
D_{calc}	=	1.47 g cm ⁻³

Intensities were collected on the diffractometer with a crystal of dimensions 1.0 × 0.6 × 0.6 mm. With Cu $K\alpha$ radiation 4302 unique integrated intensities ($3.754 > 1\sigma$) were measured for $\theta < 82^\circ$. The intensities were corrected for absorption by the method of de Meulnaer & Tompa (1965) using the program *ABSCOR* which is available in the X-RAY 63 system.

Determination and refinement of the structure

The structure was solved by the symbolic addition method (Karle & Karle, 1966) using *LSAM*, a system of computer programs for the automatic solution of centrosymmetric crystal structures written by P. Main, M. M. Woolfson and G. Germain. 249 reflexions with $E \geq 1.92$ were used and the set of phases with the highest figure of merit was used in the computation of an *E* map. The map revealed the positions of most of the non-hydrogen atoms and a difference Fourier synthesis located the remaining ones.

Positional and anisotropic temperature parameters were refined using the full-matrix least-squares program *FMLS* (Bracher & Taylor, 1967) which has been modified for use on the University of Lancaster ICL 1909 computer. The limited core store on the computer restricted the number of parameters which could be refined in one cycle to positional and anisotropic temperature parameters of ten atoms. The model was split into three bonded fragments and three runs were required to give one complete cycle of refinement. Refinement of the C, N and O atoms gave an *R* of 0.1027, and a three-dimensional ($F_o - F_c$) map gave the positions of all 21 hydrogen atoms. The hydrogen atoms were assigned isotropic temperature factors based on the anisotropic parameters of the heavy atoms to which they were bonded and further cycles of least-squares refinement reduced *R* to 0.075.

An examination of the observed and calculated structure factors showed that several of the strongest reflexions were probably affected by extinction. A correction for secondary extinction was applied using the program *ABSCOR* of the X-RAY 63 system, which follows the method of Larson (1970), using the equation

$$F_c^* = KF_c \left\{ 1 + 2R^* \left(\frac{e^2}{mc^2 V} \right)^2 \frac{\lambda^3}{\sin^2 \theta} \frac{(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)} t F_c^2 \right\}^{-1/4}$$

where R^* is the extinction parameter, related to domain size and mosaic spread, t is the mean path length and the other symbols have their usual meanings. The equation can be rewritten as

$$F_c^* = KF_c (1 + GHF_c^2)^{-1/4}$$

where $H = 2R^*(e^2/mc^2)^2$ is crystal dependent and G is only reflexion dependent for a given wavelength and crystal size. Refinement of the extinction parameter H was performed by the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) of the X-RAY 63 system. Refinement continued giving a final *R* of 0.066 and a value of 3.79 for the extinction parameter H . The maximum shift to error was 0.50 for the heavy atoms. The positional coordinates of the hydrogen atoms were refined on the last cycle. Final positional and thermal vibrational parameters are given in Tables 2 and 3, and Table 4 shows the observed and calculated structure amplitudes. For all the calculations, the atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) were used.

Discussion of the crystal structure

(a) Arrangement of the BSX molecules

In the BSX-DMF complex, 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 adja-

Table 2. Final 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)	-31148 (22)	69376 (16)	-23291 (53)
C(2)	-20565 (22)	69422 (15)	7053 (49)
C(3)	-19453 (18)	56538 (13)	8810 (43)
C(4)	-10922 (18)	46823 (13)	27468 (46)
C(5)	-15000 (22)	37174 (16)	50921 (52)
C(6)	-1858 (21)	31080 (17)	49475 (50)
C(7)	-33968 (29)	72784 (24)	-43370 (66)
C(8)	1813 (27)	24287 (21)	47465 (70)
C(9)	6915 (44)	11903 (31)	1440 (121)
C(10)	6551 (37)	4093 (39)	31785 (78)
C(11)	13541 (24)	1011 (20)	1757 (63)
N(1)	-15788 (16)	63210 (12)	6135 (39)
N(2)	-7237 (17)	63509 (14)	2192 (41)
N(3)	-15623 (15)	53147 (11)	27609 (33)
N(4)	-17661 (17)	55470 (12)	46272 (38)
N(5)	-16048 (16)	40915 (11)	31564 (37)
N(6)	-22219 (17)	38720 (12)	15725 (43)
N(7)	9048 (20)	5530 (17)	11356 (50)
O(1)	-23534 (14)	72061 (10)	-13384 (34)
O(2)	-4205 (16)	69122 (13)	-329 (41)
O(3)	-3311 (14)	58152 (12)	1959 (37)
O(4)	-21893 (15)	60682 (11)	46072 (35)
O(5)	-14891 (16)	52178 (12)	62095 (32)
O(6)	-22743 (17)	41716 (12)	-995 (37)
O(7)	-26703 (16)	33843 (11)	19562 (43)
O(8)	-10773 (13)	30785 (10)	48744 (36)
O(9)	-34902 (16)	64876 (13)	-15652 (42)
O(10)	2033 (15)	36264 (12)	51303 (41)
O(11)	16091 (18)	1768 (15)	-15203 (46)
H(1)	-25028 (260)	68223 (185)	16377 (578)
H(2)	-17052 (253)	73191 (189)	14066 (583)
H(3)	-25288 (235)	57210 (173)	8955 (531)
H(4)	-18286 (222)	53219 (174)	-3228 (547)
H(5)	-6267 (225)	46889 (173)	39281 (554)
H(6)	-9221 (222)	46765 (171)	12520 (560)
H(7)	-20199 (258)	36100 (191)	54109 (604)
H(8)	-11953 (249)	40492 (188)	61264 (613)
H(9)	-36982 (294)	70451 (222)	-52622 (699)
H(10)	-37208 (310)	75791 (241)	-42661 (721)
H(11)	-29933 (305)	74767 (252)	-49755 (738)
H(12)	920 (280)	21270 (228)	56806 (717)
H(13)	-1454 (290)	21592 (228)	35166 (723)
H(14)	7065 (286)	23699 (220)	44841 (713)
H(15)	14015 (261)	-3775 (219)	9699 (662)
H(16)	513 (418)	13276 (289)	2141 (1023)
H(17)	9628 (409)	12053 (295)	-10252 (1027)
H(18)	10531 (429)	15979 (304)	12093 (1118)
H(19)	992 (336)	4756 (336)	32219 (783)
H(20)	8877 (380)	6922 (353)	38105 (822)
H(21)	7712 (268)	-2051 (264)	37450 (591)

cent groups on the other molecule. The N...O distances are N(4)...O(10) = 2.893 (3) and N(2)...O(10) = 2.989 (4) Å, and the oxygen atom lies near to the trigonal axis of each nitrogen atom but slightly displaced towards the amine nitrogen atoms. These dimers of BSX are stacked to form columns parallel to *c*. Between the columns of BSX dimer units are channels into which the DMF molecules fit. Fig. 1 shows a projection of the structure down *c*. There are some intermolecular approaches between nitro oxygen atoms and methylene hydrogen atoms of BSX molecules within the columns and between adjacent

columns but only one of them is sufficiently short to be considered as a possible C–H···O hydrogen bond. This contact occurs between molecules related by the *c* translation and the distance is O(5)···H(4)=2.356 (36) Å. The C(3)–H(4)···O(5) angle of 146° is reasonably favourable for hydrogen bonding although the existence of such a bond is open to question (Donohue, 1968).

(b) *Arrangement of the DMF molecules*

The DMF molecules are grouped in channels between the columns of BSX dimers which run parallel to *c*. Each molecule of DMF lies so that its oxygen atom is very nearly equidistant between two nitro nitrogen atoms of adjacent groups of a BSX molecule. One of the same nitro nitrogen atoms (the central one) is also involved in the close approach to the acetyl oxygen atom of the other BSX molecule of the dimer unit. The N···O distances are N(4)···O(11)=2.891 (4) and N(6)···O(11)=2.969 (4) Å. This close approach of a DMF carbonyl oxygen to two nitrogen atoms of adjacent nitro groups in a BSX molecule is similar in all respects to the close contact of one BSX carbonyl oxygen to two nitrogen atoms of a centrosymmetrically related BSX molecule and is considered to be evidence of a definite intermolecular interaction in each case. Because this interaction is limited to pairs of BSX molecules and occurs also between BSX and DMF molecules, the complex cannot be considered to be a clathrate. In

addition, the thermal vibrational amplitudes of the atoms of the DMF molecule are not abnormally larger than those of atoms in the BSX molecule and there is no evidence of any disorder of the DMF molecules. The lone pairs of the DMF oxygen atom do not appear to be involved in the interaction; the nitro nitrogen atoms are 1.72 Å, N(4), and 1.78 Å, N(6), out of the plane in which these lone pairs would be expected to lie and the C=O···N angles are C(11)–O(11)···N(4)=94.4° and C(11)–O(11)···N(6)=136.8° against expected angles of 120° if the lone pairs are pointing at the nitrogen atoms.

Similar arrangements of BSX and solvent molecules have been found in the structures of the BSX–1,4-dioxane (1:1) and BSX–4-hydroxybutanoic acid lactone (1:1) complexes. (Cobbledick & Small, 1973*b*). A discussion of the interactions in the three complexes will be published at a later date.

(c) *Shape of the BSX molecule*

The shape of the BSX molecule is such that the central N–N bond is approximately a twofold axis. Bond lengths and angles for the BSX molecule are shown in Tables 5 and 6. Within the molecule the three nitramine groups (C₂NNO₂) and the two carboacetoxy groups (C.O.CO.CH₃) are very nearly planar. The equations of the least-squares planes through these groups and the deviations of the atoms from them are given in Table 7.

Table 3. *Thermal vibrational parameters*

The b_{ij} values and the estimated standard deviations (in parentheses) are multiplied by 10⁵. 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)	433 (15)	192 (8)	2629 (90)	192 (18)	348 (60)	70 (43)
C(2)	519 (16)	174 (7)	2265 (80)	70 (17)	336 (57)	-60 (39)
C(3)	344 (12)	159 (6)	1928 (67)	-34 (14)	230 (45)	10 (33)
C(4)	341 (12)	150 (6)	2235 (73)	8 (14)	360 (47)	-6 (35)
C(5)	480 (16)	197 (8)	2712 (87)	66 (18)	808 (60)	214 (42)
C(6)	402 (15)	255 (9)	2001 (78)	48 (19)	-2 (54)	234 (43)
C(7)	572 (22)	348 (13)	3057 (110)	266 (27)	186 (74)	498 (61)
C(8)	535 (20)	300 (11)	3644 (125)	264 (24)	212 (80)	108 (59)
C(9)	1210 (46)	444 (21)	8496 (285)	524 (48)	3572 (204)	830 (132)
C(10)	661 (27)	1024 (34)	3150 (142)	-232 (51)	956 (106)	-338 (103)
C(11)	459 (17)	333 (12)	3633 (121)	90 (23)	546 (73)	414 (62)
N(1)	324 (10)	162 (6)	2160 (65)	2 (13)	478 (42)	170 (32)
N(2)	367 (12)	258 (8)	2073 (69)	-80 (16)	412 (45)	134 (37)
N(3)	381 (11)	149 (6)	1320 (51)	18 (12)	428 (38)	-86 (27)
N(4)	436 (12)	184 (6)	1768 (62)	-78 (14)	564 (44)	-216 (32)
N(5)	403 (12)	154 (6)	2245 (62)	-28 (13)	54 (43)	-12 (30)
N(6)	440 (12)	167 (6)	2901 (79)	16 (14)	138 (49)	-268 (36)
N(7)	431 (14)	395 (11)	3124 (91)	8 (20)	590 (58)	178 (51)
O(1)	440 (10)	171 (5)	2853 (64)	32 (12)	222 (41)	318 (30)
O(2)	523 (13)	308 (8)	3582 (80)	-286 (16)	506 (51)	436 (40)
O(3)	401 (11)	318 (7)	2862 (67)	126 (14)	774 (43)	4 (36)
O(4)	519 (12)	199 (6)	2801 (64)	64 (13)	1010 (44)	-374 (31)
O(5)	687 (14)	270 (7)	1617 (51)	-18 (16)	440 (43)	22 (30)
O(6)	617 (14)	272 (7)	2455 (64)	-58 (15)	-182 (47)	-170 (34)
O(7)	517 (13)	194 (6)	4727 (93)	-174 (14)	330 (54)	-278 (38)
O(8)	392 (10)	173 (5)	3261 (68)	32 (11)	380 (40)	276 (30)
O(9)	454 (12)	249 (7)	3619 (82)	-56 (15)	230 (49)	266 (39)
O(10)	438 (11)	302 (7)	3628 (78)	-112 (14)	-186 (47)	162 (39)
O(11)	646 (15)	416 (10)	4004 (93)	244 (20)	1348 (62)	486 (49)

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

h	k	l	Observed	Calculated
1	0	0	100	100
2	0	0	100	100
3	0	0	100	100
4	0	0	100	100
5	0	0	100	100
6	0	0	100	100
7	0	0	100	100
8	0	0	100	100
9	0	0	100	100
10	0	0	100	100
11	0	0	100	100
12	0	0	100	100
13	0	0	100	100
14	0	0	100	100
15	0	0	100	100
16	0	0	100	100
17	0	0	100	100
18	0	0	100	100
19	0	0	100	100
20	0	0	100	100
21	0	0	100	100
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24	0	0	100	100
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26	0	0	100	100
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31	0	0	100	100
32	0	0	100	100
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36	0	0	100	100
37	0	0	100	100
38	0	0	100	100
39	0	0	100	100
40	0	0	100	100
41	0	0	100	100
42	0	0	100	100
43	0	0	100	100
44	0	0	100	100
45	0	0	100	100
46	0	0	100	100
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89	0	0	100	100
90	0	0	100	100
91	0	0	100	100
92	0	0	100	100
93	0	0	100	100
94	0	0	100	100
95	0	0	100	100
96	0	0	100	100
97	0	0	100	100
98	0	0	100	100
99	0	0	100	100
100	0	0	100	100

Table 4 (cont.)

C(7)-O(8)	1.436 (4)
O(8)-C(6)	1.365 (4)
C(6)-O(10)	1.186 (4)
C(6)-C(8)	1.470 (5)
C(7)-H(9)	0.84 (4)
C(7)-H(10)	0.78 (5)
C(7)-H(11)	0.88 (5)
C(2)-H(1)	0.99 (4)
C(2)-H(2)	0.99 (4)
C(3)-H(3)	0.91 (4)
C(3)-H(4)	1.05 (4)
C(4)-H(5)	0.97 (3)
C(4)-H(6)	1.02 (4)
C(5)-H(7)	0.88 (4)
C(5)-H(8)	1.01 (4)
C(8)-H(12)	0.87 (5)
C(8)-H(13)	1.03 (4)
C(8)-H(14)	0.85 (5)

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

C(7)-C(1)	1.470 (5) Å	C(5)-O(8)	1.436 (4) Å
C(1)-O(9)	1.198 (4)	O(8)-C(6)	1.365 (4)
C(1)-O(1)	1.366 (4)	C(6)-O(10)	1.186 (4)
O(1)-C(2)	1.431 (4)	C(6)-C(8)	1.470 (5)
C(2)-N(1)	1.437 (4)	C(7)-H(9)	0.84 (4)
N(1)-N(2)	1.370 (4)	C(7)-H(10)	0.78 (5)
N(2)-O(2)	1.223 (4)	C(7)-H(11)	0.88 (5)
N(2)-O(3)	1.221 (4)	C(2)-H(1)	0.99 (4)
N(1)-C(3)	1.454 (4)	C(2)-H(2)	0.99 (4)
C(3)-N(3)	1.439 (3)	C(3)-H(3)	0.91 (4)
N(3)-N(4)	1.355 (3)	C(3)-H(4)	1.05 (4)
N(4)-O(5)	1.235 (3)	C(4)-H(5)	0.97 (3)
N(4)-O(4)	1.218 (3)	C(4)-H(6)	1.02 (4)
N(3)-C(4)	1.445 (3)	C(5)-H(7)	0.88 (4)
C(4)-N(5)	1.452 (4)	C(5)-H(8)	1.01 (4)
N(5)-N(6)	1.370 (3)	C(8)-H(12)	0.87 (5)
N(6)-O(6)	1.219 (4)	C(8)-H(13)	1.03 (4)
N(6)-O(7)	1.228 (3)	C(8)-H(14)	0.85 (5)
N(5)-C(5)	1.437 (4)		

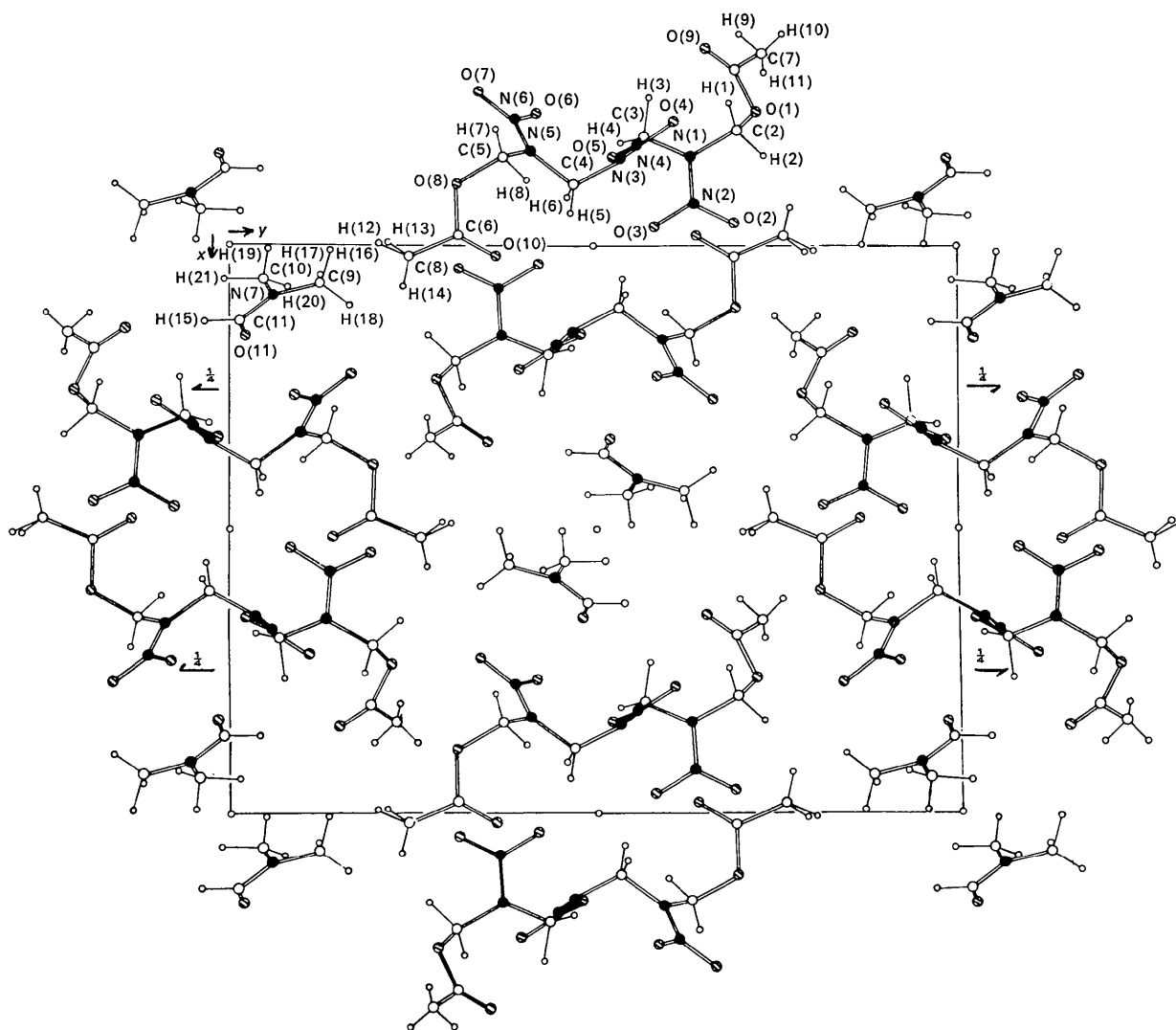
Fig. 1. The crystal structure projected down *c*.

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(10)	115 (3)°
C(7)—C(1)—O(1)	111.7 (3)	C(1)—C(7)—H(11)	118 (3)
O(9)—C(1)—O(1)	121.8 (3)	H(9)—C(7)—H(10)	99 (4)
C(1)—O(1)—C(2)	116.1 (2)	H(9)—C(7)—H(11)	106 (4)
O(1)—C(2)—N(1)	112.4 (3)	H(10)—C(7)—H(11)	100 (5)
C(2)—N(1)—C(3)	124.4 (3)	O(1)—C(2)—H(1)	118 (2)
C(2)—N(1)—N(2)	118.5 (3)	O(1)—C(2)—H(2)	103 (2)
N(2)—N(1)—C(3)	117.1 (2)	N(1)—C(2)—H(1)	102 (2)
N(1)—C(3)—N(3)	113.5 (2)	N(1)—C(2)—H(2)	114 (2)
N(1)—N(2)—O(2)	117.0 (3)	H(1)—C(2)—H(2)	106 (3)
N(1)—N(2)—O(3)	116.8 (3)	N(1)—C(3)—H(3)	105 (2)
O(2)—N(2)—O(3)	126.2 (3)	N(1)—C(3)—H(4)	112 (2)
C(3)—N(3)—C(4)	123.4 (2)	N(3)—C(3)—H(3)	111 (2)
N(4)—N(3)—C(4)	118.1 (2)	N(3)—C(3)—H(4)	104 (2)
C(3)—N(3)—N(4)	117.8 (2)	H(3)—C(3)—H(4)	111 (3)
N(3)—C(4)—N(5)	114.4 (2)	N(3)—C(4)—H(5)	108 (2)
N(3)—N(4)—O(5)	116.9 (2)	N(3)—C(4)—H(6)	102 (2)
N(3)—N(4)—O(4)	117.4 (2)	N(5)—C(4)—H(5)	103 (2)
O(5)—N(4)—O(4)	125.7 (3)	N(5)—C(4)—H(6)	112 (2)
C(4)—N(5)—C(5)	124.5 (2)	H(5)—C(4)—H(6)	119 (3)
C(4)—N(5)—N(6)	117.5 (2)	N(5)—C(5)—H(7)	109 (2)
N(6)—N(5)—C(5)	118.0 (2)	N(5)—C(5)—H(8)	103 (2)
N(5)—C(5)—O(8)	111.9 (3)	O(8)—C(5)—H(7)	104 (2)
N(5)—N(6)—O(6)	117.4 (2)	O(8)—C(5)—H(8)	117 (2)
N(5)—N(6)—O(7)	117.0 (3)	H(7)—C(5)—H(8)	112 (3)
O(6)—N(6)—O(7)	125.6 (3)	C(6)—C(8)—H(12)	118 (3)
C(5)—O(8)—C(6)	115.0 (2)	C(6)—C(8)—H(13)	113 (2)
O(8)—C(6)—O(10)	122.1 (3)	C(6)—C(8)—H(14)	122 (3)
O(8)—C(6)—C(8)	110.6 (3)	H(12)—C(8)—H(13)	94 (4)
O(10)—C(6)—C(8)	127.3 (3)	H(12)—C(8)—H(14)	106 (4)
C(1)—C(7)—H(9)	116.0 (3)	H(13)—C(8)—H(14)	99 (4)

In both carboxy groups of the molecule there is one short and one long C—O bond. Analogous bonds have been observed in ethyl carbamate (Bracher & Small, 1967) and in a number of carboxylic esters and may be due to sp^2 hybridization of the oxygen atom with an unhybridized p orbital giving partial π bonding to the carbon atom. The C—C single bond of the same group is rather short (1.470 Å) and a similar short bond has been reported in the structure of ethyl carbamate.

There are a number of short intramolecular C—H...O contacts, the shortest being 2.36 Å, which might be considered to be hydrogen bonds, but it seems more likely that they correspond to minimum repulsion distances. The geometry of the contacts is given in Table 8 and the deviation of the C—H...O angles

Table 7. Deviations of atoms from least-square 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 $-0.5850x + 0.6630y + 0.4671z = 11.1059$			
C(1)	-0.007 Å	O(9)	0.003 Å
C(7)	0.002	C(2)	0.093
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^* is $-0.0262x - 0.1026y + 0.9944z = 2.5132$			
C(6)	0.003 Å	O(10)	-0.001 Å
C(8)	-0.001	C(5)	0.024
O(8)	-0.001		
(c) Plane through atoms N(1), N(2), O(2) and O(3). Equation of the plane referred to orthogonal axes a, b, c^* is $0.1727x + 0.0753y + 0.9821z = 0.8957$			
N(1)	0.002 Å	O(3)	0.003 Å
N(2)	-0.007	C(2)	0.024
O(2)	0.003	C(3)	-0.031
(d) Plane through atoms N(3), N(4), O(4) and O(5). Equation of the plane referred to orthogonal axes a, b, c^* is $0.8363x + 0.5371y + 0.1102z = 3.6471$			
N(3)	0.002 Å	O(4)	0.003 Å
N(4)	-0.008	C(3)	-0.134
O(5)	0.003	C(4)	-0.066
(e) Plane through atoms N(5), N(6), O(6) and O(7). Equation of the plane referred to orthogonal axes a, b, c^* is $-0.7190x + 0.6203y + 0.3135z = 7.6076$			
N(5)	-0.001 Å	O(7)	-0.001 Å
N(6)	0.003	C(4)	0.053
O(6)	-0.001	C(5)	-0.078
(f) Plane through atoms C(9), C(10), C(11), N(7) and O(11). Equation of the plane referred to orthogonal axes a, b, c^* is $0.8097x + 0.3886y + 0.4398z = 1.8044$			
C(9)	0.002 Å	N(7)	-0.010 Å
C(10)	0.007	O(11)	0.006
C(11)	-0.005	H(15)	-0.144

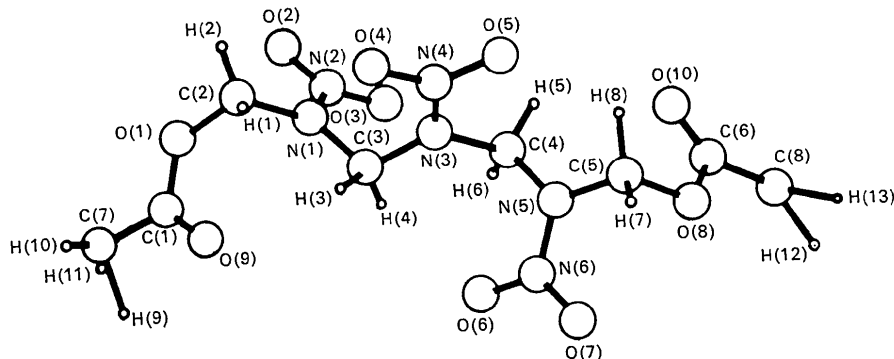


Fig. 2. The BSX molecule.

from 180° supports this view. Fig. 2 shows the conformation of the molecule and the atom labelling scheme.

Table 8. *Geometry of the intramolecular C-H...O contacts*

	Distance (Å)		Angle (°)
C(2)···O(9)	2.641 (4)	C(2)-H(1)···O(9)	88
H(1)···O(9)	2.48 (4)		
C(3)···O(9)	3.143 (4)	C(3)-H(3)···O(9)	126
H(3)···O(9)	2.53 (3)		
C(4)···O(3)	3.090 (4)	C(4)-H(6)···O(3)	112
H(6)···O(3)	2.55 (4)		
C(2)···O(4)	3.069 (4)	C(2)-H(1)···O(4)	122
H(1)···O(4)	2.42 (4)		
C(5)···O(5)	3.054 (4)	C(5)-H(8)···O(5)	125
H(8)···O(5)	2.36 (4)		
C(3)···O(6)	3.029 (4)	C(3)-H(4)···O(6)	119
H(4)···O(6)	2.39 (3)		
C(4)···O(10)	3.146 (4)	C(4)-H(5)···O(10)	121
H(5)···O(10)	2.53 (3)		
C(5)···O(10)	2.619 (4)	C(5)-H(8)···O(10)	87
H(8)···O(10)	2.46 (4)		

(d) The DMF molecule

The DMF molecule is very nearly planar and the equation of the least-squares plane through the heavy atoms and the deviations of atoms from it are shown in Table 7. The vibrational parameters of the molecule were analysed in terms of motion as a rigid body using the program *MGTLS* of Gantzel & Trueblood in which the motion is represented in terms of three tensors *T*, *L*, and *S* (Schomaker & Trueblood, 1968) for a molecule at a non-centrosymmetric site. Rigid-body parameters for the DMF molecule are given in Table 9. U_{ij} values calculated from the parameters are in reasonable agreement with the 'observed' values calculated from the corresponding b_{ij} values. 'Ob-

Table 9. *Rigid-body thermal parameters*

The direction cosines are relative to axes *a*, *b*, and *c**

Principal axes of <i>L</i>				
r.m.s. amplitude	Direction cosines ($\times 10^3$)			
13.6°	822	-178	-540	
7.0	545	518	659	
5.8	162	-838	522	
Principal axes of reduced <i>T</i>				
r.m.s. amplitude	Direction cosines ($\times 10^3$)			
0.28 Å	149	763	630	
0.23	-410	626	-662	
0.21	-901	-158	404	
Symmetrized screw tensor, <i>S</i>				
	$\begin{pmatrix} 412 & 484 & 100 \\ & -543 & 662 \\ & & 129 \end{pmatrix} \times 10^5 \text{ rad } \text{Å}$			

served' and calculated U_{ij} values are tabulated in Table 10. The r.m.s. ΔU_{ij} is 0.0032 Å² compared with an estimated σU_{ij} value of 0.0028 Å² calculated from the standard deviations of the b_{ij} values. The atomic coordinates were corrected for the librational motion indicated by the model and uncorrected and corrected bond lengths and angles are listed in Tables 11 and 12.

Table 11. *Bond distances and their standard deviations for the N,N-dimethylformamide molecule*

	Before libration correction	After libration correction
C(9)-N(7)	1.432 (7) Å	1.463 Å
C(10)-N(7)	1.439 (6)	1.461
N(7)-C(11)	1.327 (5)	1.351
C(11)-O(11)	1.211 (5)	1.230
C(11)-H(15)	1.07 (4)	
C(9)-H(16)	1.03 (7)	
C(9)-H(17)	0.90 (7)	
C(9)-H(18)	1.15 (6)	
C(10)-H(19)	0.87 (5)	
C(10)-H(20)	0.75 (6)	
C(10)-H(21)	1.27 (5)	

Table 12. *Bond angles and their standard deviations for the N,N-dimethylformamide molecule*

	Before libration correction	After libration correction
C(9)-N(7)-C(10)	120.4 (5)°	120.9°
C(9)-N(7)-C(11)	119.4 (4)	119.7
C(10)-N(7)-C(11)	120.2 (4)	119.4
N(7)-C(11)-O(11)	125.4 (4)	124.5
O(11)-C(11)-H(15)	122 (2)	
N(7)-C(11)-H(15)	112 (2)	
N(7)-C(9)-H(16)	112 (3)	
N(7)-C(9)-H(17)	107 (4)	
N(7)-C(9)-H(18)	107 (3)	
H(16)-C(9)-H(17)	125 (5)	
H(16)-C(9)-H(18)	100 (5)	
H(17)-C(9)-H(18)	103 (5)	
N(7)-C(10)-H(19)	112 (3)	
N(7)-C(10)-H(20)	100 (4)	
N(7)-C(10)-H(21)	114 (2)	
H(19)-C(10)-H(20)	106 (6)	
H(19)-C(10)-H(21)	104 (5)	
H(20)-C(10)-H(21)	121 (5)	

The authors wish to thank Dr T. N. Huckerby for the n.m.r. analysis, Dr D. Stubbley for the thermogravimetric analysis, the Procurement Executive, Ministry of Defence, for a grant in support of this work, Dr B. H. Bracher for a card deck of the program *FMLS*, Professor K. N. Trueblood for a listing of the program

Table 10. *Observed and calculated values of ($U_{ij} \times 10^4$) (Å²)*

	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)	526	519	661	652	745	721	53	39	41	58	132	182
C(10)	1250	1243	881	847	1742	1774	370	421	663	644	265	231
C(11)	740	751	2032	1995	646	620	-165	-172	155	133	-108	-31
N(7)	488	489	784	851	640	665	-1	-36	65	82	57	-2
O(11)	699	701	825	838	821	814	168	172	230	238	155	121

MGTLs and Dr G. Germain, Dr P. Main and Professor M. M. Woolfson for a card deck of the program LSAM.

References

- BRACHER, B. H. & SMALL, R. W. H. (1967). *Acta Cryst.* **23**, 410–418.
- BRACHER, B. H. & TAYLOR, R. I. (1967). U.K.A.E.A. Research Report AERE-R5478.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CLARINGBULL, G. F. & SMALL, R. W. H. (1971). *Acta Cryst.* **B27**, 863–864.
- COBBLEDICK, R. E. & SMALL, R. W. H. (1973a). *Acta Cryst.* **B29**, 640–641.
- COBBLEDICK, R. E. & SMALL, R. W. H. (1973b). To be published.
- DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*. Edited by A. RICH & N. DAVIDSON, p. 459. San Francisco: Freeman.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
- LARSON, A. C. (1970). *Crystallographic Computing*. Edited by F. R. AHMED, pp. 291–294. Copenhagen: Munksgaard.
- MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SMALL, R. W. H. & TRAVERS, S. (1961). *J. Sci. Instrum.* **38**, 205–206.

Acta Cryst. (1973). **B29**, 1666

The Crystal Structure of Mercury(I) Orthoarsenate

BY B. KAMENAR AND B. KAITNER

Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, P.O. Box 153, 41001 Zagreb, Yugoslavia

(Received 27 February 1973; accepted 11 March 1973)

The crystal structure has been determined by single-crystal three-dimensional X-ray analysis. There are two formula units of $(\text{Hg}_2)_3(\text{AsO}_4)_2$ in the monoclinic unit cell of dimensions $a=8.73$, $b=5.08$, $c=15.64$ Å, $\beta=128.4^\circ$ and space group $P2_1/c$. The structure is built up of Hg_2^{2+} and AsO_4^{3-} ions in such a way that three of the four arsenate oxygen atoms are bonded to three different Hg–Hg pairs, thus forming puckered layers. An effectively tetrahedral coordination about the mercury atoms is established by one mercury atom from the same Hg_2^{2+} pair, one oxygen atom at 2.16 to 2.23 Å, and two other oxygen atoms at 2.42 to 2.71 Å. The Hg–Hg–O bonds deviate from collinearity by 23 to 34°. One As–O bond length is longer (1.78 Å) than the other three (mean value 1.68 Å).

Introduction

This investigation is part of a research programme to extend the data on the structural chemistry of mercury(I) compounds, because little is known even now about the coordination of the mercury atom in these compounds. There are only 15 known structures of mercury(I) compounds and about two thirds of these have been solved from three-dimensional data.

In all known structures with oxygen atoms linked to mercury, as in mercury(I) sulphate, selenate (Dorm, 1969), bromate (Dorm, 1967), *o*-phthalate (Lindh, 1967) and trifluoroacetate (Grdenić & Sikirica, 1973), linear or almost linear O–Hg–Hg–O chains or groups are found. The linear oxonium ion $\text{H}_2\text{O–Hg–Hg–OH}_2$ is present in hydrated salts, as in mercury(I) nitrate (Grdenić, 1956), hexafluorosilicate (Dorm, 1971a), and perchlorate (Johansson, 1966). If one member of the Hg–Hg pair is linked to a different ligand a linear Hg–Hg–O grouping is formed, as in 1,10-phenanthroline-mercury(I) nitrate (Elder, Halpern & Pond, 1967). In the present structure a puckered-layer structure in

which one arsenate ion links three Hg_2^{2+} pairs has been found.

Experimental

Red-brown prismatic crystals were prepared by the reaction between aqueous mercury(I) nitrate solution and arsenic acid (Guérin & Boulitrop, 1951). The system is monoclinic, $a=8.73 \pm 0.02$, $b=5.08 \pm 0.01$, $c=15.64 \pm 0.03$ Å, and $\beta=128.4 \pm 0.3^\circ$. The cell parameters were determined from oscillation and Weissenberg photographs. The systematic absence of reflexions $h0l$ for l odd and $0k0$ for k odd uniquely determined the space group as $P2_1/c$. The cell contains two formula units $(\text{Hg}_2)_3(\text{AsO}_4)_2$; the pycnometrically measured density was 9.05 g cm^{-3} and the calculated density was 9.06 g cm^{-3} . Three-dimensional intensity data ($0kl \dots 7kl$, $h0l \dots h4l$, and $hk0 \dots hk14$) were obtained on an integrating Weissenberg camera using the multiple-film technique and nickel-filtered Cu *K* radiation. The intensities of 1137 independent observed reflexions were estimated by means of a microdensitometer, corrected for Lorentz and polarization effects