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References

ANDERSSON, G. (1956). *Acta Chem. Scand.* **10**, 623.
ANDERSSON, S., COLLÉN, B., KRUUSE, G., KUYLENSTIERNA, U., MAGNÉLI, A., PESTMALIS, H. & ÅSBRINK, S. (1957*a*). *Acta Chem. Scand.* **11**, 1653.
ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957*b*). *Acta Chem. Scand.* **11**, 1641.
ÅSBRINK, S., BLOMQVIST, G. & WESTMAN, S. (1959). *Ark. Kemi, Min. Geol.* (In press.)
ÅSBRINK, S. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1606.
BAUR, W. H. (1956). *Acta Cryst.* **9**, 515.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
FILONENKO, N. E., KUDRYAVTSEV, V. I. & LAVROV, I. V. (1952). *Doklady Akad. Nauk. S.S.S.R.* **86**, 561.
HAMBLING, P. G. (1953). *Acta Cryst.* **6**, 98.
HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.
LEUNG, Y. C., MARSH, R. E. & SCHOMAKER, V. (1957). *Acta Cryst.* **10**, 650.
LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, p. 277. London: Bell.
MAGNÉLI, A. (1948). *Acta Chem. Scand.* **2**, 501.
MAGNÉLI, A. & ANDERSSON, G. (1955). *Acta Chem. Scand.* **9**, 1378.
MARINDER, B.-O. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1635.
NAYLOR, B. F. (1946). *J. Amer. Chem. Soc.* **68**, 1077.
VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**. 303.
WESTMAN, S., BLOMQVIST, G. & ÅSBRINK, S. (1959). *Ark. Kemi, Min. Geol.* (In press.)
WESTMAN, S., NORDMARK, C. & SUNDHOLM, A. (To be published.)
ZHDANOV, G. S. & RUSAKOV, A. V. (1954). *Trudy Inst. Krist., Akad. Nauk S.S.S.R.* **9**, 165.

Acta Cryst. (1959). **12**, 581

The Crystal Structure of the Dipotassium Salt of Methylene-*bis*-Nitrosohydroxylamine, $CH_2(N_2O_2K)_2$

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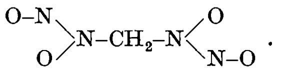
Crystals of the dipotassium salt of methylene-*bis*-nitrosohydroxylamine are orthorhombic, having the unit-cell dimensions $a_0 = 26{\cdot}40$ Å, $b_0 = 12{\cdot}81$ Å, and $c_0 = 3{\cdot}95$ Å. The space group is *Fdd*2, and there are eight molecules per unit cell.

The structure was deduced and refined by Fourier and least-squares methods. The anion has the following configuration:



There is a two-fold axis through the methylene group. The N–CH_2–N bond angle is slightly less than tetrahedral. Resonance occurs among the N–N and N–O bonds, and accordingly the CN_2O_2 grouping is nearly planar. The CH_2–N bond is significantly longer than the usual carbon–nitrogen single bond length.

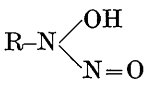
Introduction

Salts of methylene-*bis*-nitrosohydroxylamine were first prepared by Wilhelm Traube (1894) by the reaction of nitric oxide with acetone in the presence of alkali:

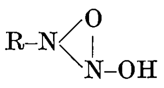
$$2\ NO+CH_3.CO.CH_3+3\ OH^- \rightarrow CH_2(N_2O_2)_2^{--}+CH_3COO^-+2\ H_2O.$$

During his extensive investigations Traube (1898) prepared many compounds containing the grouping $-N_2O_2H$, usually as salts since the free acids are quite unstable. Among the compounds he describes is the monopotassium salt of methylene-*bis*-nitrosohydroxylamine, but not the dipotassium salt. The disodium salt is ordinarily obtained as the monohydrate; the dipotassium salt, however, is anhydrous.

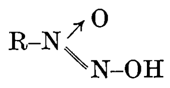
A number of possible structures were proposed by Traube (1895, 1898) for the $-N_2O_2H$ grouping:



I



II

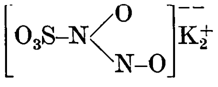


III

$$R{-}N{=}N{-}O{-}OH.$$

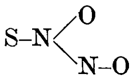
IV

Structure II was favored by Traube. However, the results of the X-ray analysis reported here show that either structure I or structure III is the correct one. This result is in agreement with that obtained by Cox, Jeffrey & Stadler (1949) in the analysis of the structure of potassium dinitrososulfite:



$$\left[O_3S{-}N\begin{matrix}\diagup O\\ \diagdown N{-}O\end{matrix}\right]^{--} K_2^{+}$$

In this ion the atoms are bonded tetrahedrally to the sulfur atom, but the



$$S{-}N\begin{matrix}\diagup O\\ \diagdown N{-}O\end{matrix}$$

grouping is planar.

Experimental

Crystals of the dipotassium salt were grown by slow evaporation of an aqueous solution at room temperature. They were formed as long needles or prisms. The rotation and Weissenberg photographs about the needle axis showed an orthorhombic unit cell having the dimensions (λ of Cu $K\alpha$ = 1·5418 Å):

$$a_0 = 26{\cdot}40 \pm 0{\cdot}13,\ b_0 = 12{\cdot}81 \pm 0{\cdot}06,\ c_0 = 3{\cdot}95 \pm 0{\cdot}02\ \text{Å}.$$

The observed extinctions uniquely determined the space group as $Fdd2$ (hkl present only with $h+k = 2n$ and $k+l = 2n$, $0kl$ present only with $k+l = 4n$, and $h0l$ present only with $h+l = 4n$). The density, obtained by flotation in a mixture of methylene iodide and bromobenzene, was found to be 2·11 g.cm^{-3}. The calculated density for eight molecules of $CH_2(N_2O_2K)_2$ per unit cell is 2·110 g.cm^{-3}. As the general positions in this space group are 16-fold, the molecule probably has a 2-fold axis.

The intensity data required for the structure analysis were estimated visually from equi-inclination Weissenberg photographs of the $hk0$, $hk1$, and $hk2$ reflections. These data represent about 70% of the reflections accessable to the Cu $K\alpha$ radiation used.

Determination of the structure

The x and y parameters

After correcting the intensities for the Lorentz and polarization factors, a Patterson projection was calculated with the $hk0$ data. The potassium ion was located approximately at $x = 0{\cdot}074$, $y = 0{\cdot}250$ from the vector peaks between ions related by the glide planes. Since the y parameter of the potassium ion is $\frac{1}{4}$, it will contribute only to reflections for which $h+k = 4n$. The signs of 51 reflections of this type were determined and a Fourier projection was calculated. This projection immediately gave rough positions for the light atoms. The first complete Fourier projection, calculated with 83 terms, showed that the y parameter of the potassium ion was not exactly $\frac{1}{4}$, but was somewhat larger. The final Fourier projection, Fig. 1(a), was calculated with 101 of the 103 observed reflections.

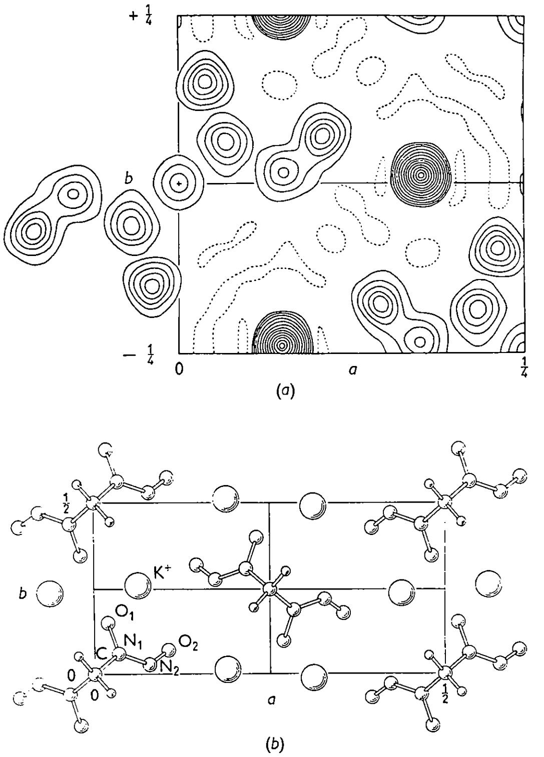


Fig. 1. (a) Final Fourier projection of $CH_2(N_2O_2K)_2$ on (001). The contour interval is 2 electrons per Å^2. The zero contour is broken. (b) Projection of one quarter of the unit cell on (001). The identifying numbers are shown for the atoms of the asymmetric unit.

The z parameters

Using reasonable values for the C–N, N–N, and N–O bond lengths and angles and for the potassium oxygen contacts, the approximate z parameters of a

Table 1. *Final parameters of the atoms, peak heights, and the standard deviations of the atomic coordinates*

Atom	X	Y	Z	ϱ_0 (e.Å^{-3})	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
K^+	0·0746	0·2608	0·000	40·5	0·0007	0·0007	0·0013
O_1	0·0194	0·1510	0·427	13·3	0·003	0·003	0·004
O_2	0·1040	0·0714	0·238	13·2	0·003	0·003	0·004
N_1	0·0343	0·0613	0·518	10·8	0·003	0·003	0·004
N_2	0·0772	0·0157	0·456	10·7	0·003	0·003	0·006
$C(H_2)$	0·0000	0·0000	0·751	7·9	0·004	0·004	0·007

three-dimensional trial structure were calculated. Because the c-axis is the polar axis in this space group, there are two possible arrangements of the molecules with respect to the positive direction of the c-axis. Calculating the structure amplitudes of the $hk1$ reflections for these two arrangements showed which one was correct. The z parameters were then further improved by a series of least-squares calculations, using the $hk1$ and $hk2$ data. The final refinements of all parameters were made by calculating F_o and F_c Fourier syntheses and making backshift corrections. The final parameters are listed in Table 1.

Accuracy

The standard deviations of the atomic coordinates and of important interatomic distances were calculated by the method of Cruickshank (1949). The values obtained are listed in Tables 1 and 2. Following the suggestion of Roof (1956) the standard deviations have been divided by the ratio of the actual number of reflections used in the three-dimensional Fouriers to the number accessable to Cu $K\alpha$ radiation to correct for the effect of the reduced number of reflections used. The structure amplitudes were calculated using an isotropic temperature correction, $\exp[-B(\sin\theta/\lambda)^2]$, with $B = 1{\cdot}65$ Å^2. The final percentage discrepancy is 8·7 for all observed reflections used in calculating the three-dimensional Fouriers. The reflections (111), (311), (511), (911), and (202), were omitted from these calculations. Calculations support the belief that these reflections have been weakened by extinction.

Discussion

The packing of the molecules in the structure is shown in Fig. 1(*b*), which also indicates the numbering system for identifying the atoms of the asymmetric unit. The Figure shows one-fourth of a unit cell projected along the short c_0 axis.

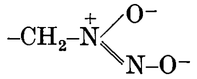
Table 2. *Interatomic distances and bond angles*

	d	σ
$C(H_2)–N_1$	1·512 Å	0·007 Å
$N_1–N_2$	1·297	0·004
$N_1–O_1$	1·266	0·004
$N_2–O_2$	1·323	0·006
$O_1 \cdots O_2$	2·566 Å	0·004 Å
$C(H_2)–N_1–O_1$	117·2°	
$C(H_2)–N_1–N_2$	113·8°	
$O_1–N_1–N_2$	128·8°	
$N_1–N_2–O_2$	110·2°	
$N_1–C(H_2)–N_1$	104·9°	
$K^+ \cdots O_1$	2·64 Å	
$K^+ \cdots O_2$	2·72	
$K^+ \cdots O_1'$	2·74	
$K^+ \cdots O_2''$	2·82	
$K^+ \cdots (O_2'')_1$	2·87	
$K^+ \cdots (O_1)_1$	3·04	
$K^+ \cdots N_2'''$	3·27	

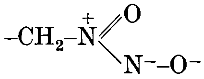
Table 2 shows the dimensions of the anion. The nitrogen–nitrogen and nitrogen–oxygen distances indicate that resonance must be occurring among these bonds. Using Pauling's relation between bond length and double-bond character,

$$r = r_1-(r_1-r_2)(3x)/(2x+1)$$

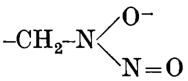
the double bond character in each bond was estimated. It is possible to write only three resonance structures for this ion:



A



B



C

By weighting structure *A* at 50%, structure *B* at 33%, and structure *C* at 17% and applying Pauling's relation (using 1·47 Å for the N–N single bond, 1·43 Å for the N–O single bond, 1·24 Å for the N=N double bond and 1·15 Å for the N=O double bond), the following bond lengths are calculated:

Bond	Double bond character	Length (obs.)	Length (calc.)
$N_1–N_2$	0·50	1·297 Å	1·298 Å
$N_1–O_1$	0·33	1·266	1·263
$N_2–O_2$	0·17	1·323	1·323

Structure *B* violates the adjacent charge rule by having negative charges on both N_2 and O_2; however, it is probable that the potassium ion at a distance of 3·27 Å from N_2 and with nearly the same z parameter will stabilize this resonance form.

The $CH_2–N_1$ bond length was found to be 1·512 Å with a standard deviation of 0·007 Å. This is greater by 0·042 Å than the usual value of 1·47 Å for a carbon–nitrogen single bond. Donohue, Lavine & Rollett (1956) have pointed out that the $C–NH_3^+$ bond length in a number of amino acids has an average value of 1·505 Å. The above result is in excellent agreement with this average. This emphasizes the importance of the resonance structures which place a positive charge on N_1.

A least-squares plane was calculated through the positions of the five atoms in half of the molecule. In the normal form, the equation of this plane is,

$$0{\cdot}4382X+0{\cdot}4237Y+0{\cdot}7928Z = 2{\cdot}366\,.$$

The average deviation of the atoms from this plane is 0·023 Å, the greatest deviation being 0·04 Å for N_2. The dihedral angle between the planes defined by the two halves of the molecule is 75·1°.

The close approach of atoms O_1 and O_2 (2·566 Å) suggests that the deviations from planarity may be caused by steric repulsion. The equation of the plane defined by CH_2, N_1, and N_2 is, *Table of observed and calculated structure amplitudes*

Phases are given only for the (*hk*0) reflections

A negative sign in the $|F_o|$ column indicates the maximum possible value of a non-observed reflection

hkl	$\|F\|_o$	F_c
000	—	816
400	13	−5
800	117	−132
12,0,0	191	176
16,0,0	16	−11
20,0,0	137	−141
24,0,0	−7	−4
28,0,0	102	100
32,0,0	63	−57
220	11	−16
420	104	−120
620	119	125
820	67	−66
10,2,0	56	50
12,2,0	167	−146
14,2,0	184	−162
16,2,0	13	7
18,2,0	71	66
20,2,0	15	−16
22,2,0	71	70
24,2,0	−7	−2
26,2,0	36	−32
28,2,0	18	20
30,2,0	19	21
32,2,0	−5	−2
040	219	227
240	187	−177
440	103	−104
640	13	1
840	226	−212
10,4,0	52	46
12,4,0	184	166
14,4,0	−6	−7
16,4,0	80	81
18,4,0	34	32
20,4,0	107	−100
22,4,0	34	32
24,4,0	65	63
26,4,0	39	41
28,4,0	95	90
30,4,0	44	−40
32,4,0	42	−35
260	38	−44
460	14	13
660	196	192
860	5	−2
10,6,0	10	7
12,6,0	32	−36
14,6,0	23	−19
16,6,0	73	70
18,6,0	24	24
20,6,0	30	26
22,6,0	38	39
24,6,0	6	−7
26,6,0	75	−57
28,6,0	13	13
30,6,0	36	−31
080	93	93
280	80	−79
480	10	−2
680	79	−75
880	102	−103
10,8,0	50	50
12,8,0	139	131
14,8,0	54	−52
16,8,0	82	80
18,8,0	74	−79
20,8,0	87	−93
22,8,0	40	43
24,8,0	32	33
26,8,0	7	10
28,8,0	31	27
2,10,0	93	−88
4,10,0	75	76
6,10,0	43	49
8,10,0	25	−34
10,10,0	7	4
12,10,0	11	8
14,10,0	17	−15
16,10,0	12	11
18,10,0	51	52
20,10,0	6	4
22,10,0	48	54
24,10,0	40	−36
26,10,0	21	−18
0,12,0	91	98
2,12,0	32	−33
4,12,0	12	−17
6,12,0	−7	−5
8,12,0	28	−32
10,12,0	107	120
12,12,0	50	59
14,12,0	−6	5
16,12,0	20	21
18,12,0	55	−59
20,12,0	36	−36
22,12,0	45	49
2,14,0	13	15
4,14,0	42	48
6,14,0	42	41
8,14,0	15	−20
10,14,0	18	25
12,14,0	28	−26
14,14,0	42	−47
16,14,0	13	18
0,16,0	27	44
2,16,0	39	−63
4,16,0	6	−12
6,16,0	8	−16
8,16,0	9	−17
111	69	122
311	94	154
511	101	142
711	96	103
911	146	198
11,1,1	112	129
13,1,1	38	38
15,1,1	11	5
17,1,1	81	88
19,1,1	52	57
21,1,1	51	54
23,1,1	80	87
25,1,1	30	25
27,1,1	19	12
29,1,1	44	42
31,1,1	42	35
33,1,1	31	31
131	95	109
331	118	165
531	153	218
731	23	16
931	65	75
11,3,1	82	95
13,3,1	28	27
15,3,1	63	66
17,3,1	85	93
19,3,1	30	33
21,3,1	58	55
23,3,1	80	80
25,3,1	59	55
27,3,1	32	28
29,3,1	49	39
31,3,1	45	39
151	77	80
351	92	100
551	65	69
751	120	129
951	42	39
11,5,1	96	90
13,5,1	55	53
15,5,1	77	83
17,5,1	102	106
19,5,1	54	54
21,5,1	42	47
23,5,1	29	27
25,5,1	45	37
27,5,1	18	14
29,5,1	43	38
31,5,1	24	17
171	65	71
371	134	140
571	75	65
771	44	43
971	46	44
11,7,1	77	89
13,7,1	14	12
15,7,1	73	71
17,7,1	88	88
19,7,1	15	10
21,7,1	14	11
23,7,1	67	59
25,7,1	61	50
27,7,1	37	32
29,7,1	59	57
191	52	56
391	53	51
591	80	82
791	48	51
991	44	44
11,9,1	73	76
13,9,1	66	72
15,9,1	70	66
17,9,1	36	34
19,9,1	17	18
21,9,1	22	21
23,9,1	38	32
25,9,1	42	37
27,9,1	35	33
1,11,1	61	72
3,11,1	33	36
5,11,1	39	39
7,11,1	54	48
9,11,1	65	68
11,11,1	71	76
13,11,1	49	47
15,11,1	27	25
17,11,1	53	51
19,11,1	40	36
21,11,1	14	18
23,11,1	42	40
1,13,1	67	60
3,13,1	39	30
5,13,1	49	48
7,13,1	32	31
9,13,1	18	20
11,13,1	15	11
13,13,1	47	45
15,13,1	25	26
17,13,1	25	27
19,13,1	37	38
1,15,1	25	25
3,15,1	27	22
5,15,1	54	51
7,15,1	37	35
9,15,1	27	31
11,15,1	27	31
202	116	180
602	122	126
10,0,2	76	77
14,0,2	140	137
18,0,2	135	133
22,0,2	86	82
26,0,2	94	80
30,0,2	23	17
022	142	156
222	34	37
422	55	64
622	68	78
822	51	55
10,2,2	54	56
12,2,2	104	110
14,2,2	30	32
16,2,2	52	52
18,2,2	26	28
20,2,2	49	42
22,2,2	24	22
24,2,2	11	12
26,2,2	12	10
28,2,2	55	48
30,2,2	18	16
242	65	72
442	49	48
642	196	200
842	46	44
10,4,2	19	16
12,4,2	63	68
14,4,2	108	107
16,4,2	44	44
18,4,2	58	61
20,4,2	34	35
22,4,2	62	57
24,4,2	46	43
26,4,2	80	75

Table (*cont.*)

hkl	$\|F\|_o$	F_c	*hkl*	$\|F\|_o$	F_c	*hkl*	$\|F\|_o$	F_c	*hkl*	$\|F\|_o$	F_c
28,4,2	22	19	26,6,2	12	10	0,10,2	89	92	6,12,2	51	50
30,4,2	7	9	28,6,2	52	49	2,10,2	23	17	8,12,2	80	78
						4,10,2	28	30	10,12,2	12	15
062	84	87	282	41	49	6,10,2	46	44	12,12,2	43	42
262	37	43	482	83	89	8,10,2	37	36	14,12,2	49	48
462	27	29	682	124	135	10,10,2	32	33	16,12,2	41	38
662	26	22	882	30	35	12,10,2	38	36	18,12,2	36	35
862	89	88	10,8,2	27	30	14,10,2	9	5			
10,6,2	52	44	12,8,2	17	21	16,10,2	10	13	0,14,2	31	39
12,6,2	58	52	14,8,2	72	71	18,10,2	35	34	2,14,2	31	33
14,6,2	18	22	16,8,2	60	61	20,10,2	59	50	4,14,2	25	28
16,6,2	41	42	18,8,2	32	28	22,10,2	43	41	6,14,2	22	24
18,6,2	31	30	20,8,2	12	13				8,14,2	15	15
20,6,2	73	65	22,8,2	58	53	2,12,2	30	26	10,14,2	28	32
22,6,2	15	11	24,8,2	43	38	4,12,2	53	57	12,14,2	27	33
24,6,2	53	44	26,8,2	33	30						

$$0{\cdot}4058X+0{\cdot}4593Y+0{\cdot}7901Z = 2{\cdot}344 \, .$$

Atom O_1 deviates $+0{\cdot}085$ Å from this plane (on the side away from the origin), and atom O_2 deviates $-0{\cdot}065$ Å from the plane (on the side towards the origin). The angle O_1–N_1–N_2 is 129°, more than 10° larger than any other bond angle. This also suggests that steric effects occur here.

Table 2 lists distances of the potassium ions to the surrounding atoms. These are generally in agreement with the distances found in other similar potassium salts such as potassium dinitrososulfite (Cox, Jeffrey & Stadler, 1949) and dipotassium nitroacetate (Sutor, Llewellyn & Maslen, 1954).

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References

Cox, E. G., Jeffrey, G. A. & Stadler, H. P. (1949). *J. Chem. Soc.* p. 1783.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Donohue, J., Lavine, L. R. & Rollett, J. S. (1956). *Acta Cryst.* **9**, 655.

Roof, R. B., Jr. (1956). *Acta Cryst.* **9**, 781.

Sutor, D. J., Llewellyn, F. J. & Maslen, H. S. (1954). *Acta Cryst.* **7**, 145.

Traube, W. (1894). *Ber. dtsch. chem. Ges.* **27**, 1507.

Traube, W. (1895). *Ber. dtsch. chem. Ges.* **28**, 2297.

Traube, W. (1898). *Liebigs Ann.* **300**, 81.

Acta Cryst. (1959). **12**, 585

The Crystal Structures of the Dibromide and Di-iodide of 5:10-dihydro-5:10-dimethylarsanthren

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The dibromide of 5:10-dihydro-5:10-dimethylarsanthren crystallises in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a = 11{\cdot}27$, $b = 9{\cdot}70$, $c = 14{\cdot}87$ Å, while the di-iodide crystallises in the monoclinic space group $P2_1/c$ with $a = 10{\cdot}63$, $b = 9{\cdot}94$, $c = 17{\cdot}02$ Å, $\beta = 108{\cdot}6°$. The coordinates of the heavy atoms were determined from the $h0l$ and $0kl$ sharpened Patterson projections and refined by Fourier syntheses; coordinates for the carbon atoms of the arsanthren ring and probable coordinates for the methyl groups in the dibromide were obtained from difference syntheses. The stereochemistry is similar for the two molecules; they are folded about the As–As axis and the two halogen atoms are disposed one on each side of one arsenic atom, the line joining the halogen atoms being at right angles to the plane which contains the three As–C bonds of this arsenic atom. The valencies of the other arsenic atom are probably non-planar, as in other 3-covalent arsenic compounds, though a planar configuration cannot be definitely excluded. The As–Br and As–I bonds are significantly longer than covalent bonds and may be either ionic or intermediate between ionic and covalent.

1. Introduction

The crystal structures of the dibromide and di-iodide of 5:10-dihydro-5:10-dimethylarsanthren (see Fig. 1) have been investigated in order to determine the nature of the As–Br and As–I bonds, and if possible the stereochemistry of the molecule.

In a chemical investigation of these compounds Jones & Mann (1955) found that all the bromine in an aqueous-methanolic solution of the dibromide is ionic and hence can be estimated volumetrically. In solution, the properties of the di-iodide indicate that it may exist as an equilibrium mixture of the ionic