$NH_4[Eu(mal)_2]\cdot 3H_2O$ (mal = $C_4H_2O_4^{2-}$) Calc. Eu 33,61 C 21,25 H 3,12 N 3,10%
Tr. ,, 33,65 ,, 21,34 ,, 3,22 ,, 3,17%

$NH_4[Sm(mal)_2]\cdot 3H_2O$ Calc. Sm 33,27% Tr. Sm 33,49%

$NH_4[Nd(mal)_2]\cdot 3H_2O$ Calc. Nd 32,46 N 3,15% Tr. Nd 32,54 N 3,11%

$NH_4[Pr(mal)_2]\cdot 3H_2O$ Calc. Pr 31,94% Tr. Pr 31,87%

$NH_4[La(mal)_2]\cdot 3H_2O$ Calc. La 31,64 N 3,19% Tr. La 31,71 N 3,16%

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219. Arsenomethane Polymer: A Ladder Structure

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(11. IX. 70)

Summary. Purple arsenomethane crystallises in the orthorhombic system, space group *Ima*2 (C^{22}_{2v}) with $a = 5.81$, $b = 5.79$, $c = 13.64$ Å and 8 units of CH_3As in the cell. The structure is polymeric, the arsenic atoms lying on infinite coplanar ladders parallel to *a*. The distance between two arsenic atoms on one rung of the ladder is 2.4 Å, the distance between two arsenic atoms on the same upright and adjacent rungs is 2.9 Å, and the shortest distance between two arsenic atoms in neighbouring ladders is 3.4 Å. Each arsenic atom is bonded to one methyl group (1.97 Å), and along the ladder upright or on any one rung these methyl groups lie on alternate sides of the ladder.

Two recent papers describe the synthesis of a purple, insoluble, form of arsenomethane $(CH_3As)_x$, m.p. 204° [1]. The platelike crystals of this form, typical size 0.15 × 0.15 × 0.05 mm, appear black in polarised light and dark red when viewed between crossed Nichols.

An *X*-ray analysis [2] of the yellow (m.p. 12°) form of arsenomethane showed that the crystals are built up from discrete $(CH_3As)_5$ molecules containing non-planar equilateral five-membered arsenic rings. However, an *X*-ray powder investigation [3] of the red microcrystalline arsenomethane failed to reveal the detailed structure of this form.

Crystal Data. Purple arsenomethane $(CH_3As)_x$, molecular weight of monomer 89.96, orthorhombic, $a = 5.81$, $b = 5.79$, $c = 13.64$ Å, $U = 458.9$ Å^3, $Z = 8$ (CH_3As), $D_m = 2.45$, $D_c = 2.60$, space group $Ima2$ (No. 46, C_{2v}^{22}). The d spacings were obtained from a powder photograph and are shown in Table 1. X-ray photographs from all 'single' crystals examined showed split reflections. The degree of splitting varied from crystal to crystal. The best crystal found showed very little splitting on the zero $0kl$ layer *Weissenberg* photograph but quite serious splitting on the first and second layers.

Table 1. *The* d *spacings of 'purple' arsenomethane from a powder photograph*
The intensities are rough visual estimates

d	I_0	d	I_0	d	I_0
6.899	100	2.897	30	2.052	3
5.356	10	2.672	15	1.919	7
4.077	1	2.628	5	1.788	15
3.552	5	2.274	15	1.710	5
3.470	2	2.213	5	1.475	3
3.396	15	2.175	2	1.453	3

Intensity Measurements. Oscillation and *Weissenberg* photographs taken about [a] show that the intensities of corresponding $0kl$ and $2kl$ reflections are very similar and are strong, while the $1kl$ reflections are rather weak. Because the reflections were split, only the 53 $0kl$ intensities with $\sin\theta/\lambda < 0.59$ Å^{-1} were measured on a linear diffractometer [4] equipped with balanced filters. Because of this shortage of data, the analysis is of limited accuracy. The high linear absorption coefficient ($\mu_{Mo-K\alpha} = 151$ cm^{-1}) and the unfavourable shape of the crystal (0.15 × 0.15 × 0.05 mm) persuaded us to apply a *Busing-Levy* [5] type absorption correction to the measured intensities.

Structure Analysis and Refinement. The $0kl$ projection was solved by *Patterson* and *Fourier* methods and then refined by a least-squares process till the conventional R factor was 0.061. During this process it became obvious, mainly from packing considerations, that there were two independent methyl groups in the unit cell, both lying on the mirror planes perpendicular to a. The strong similarity of the $0kl$ and $2kl$ photographs together with the weakness of the $1kl$ reflections suggest two possibilities for the placing of the arsenic atoms, one with arsenic in a general position with X_{As} close to zero and the second with two independent arsenic atoms lying on the mirror planes perpendicular to a. The second possibility, with the arsenic atoms on special positions, was then chosen for two reasons; it made more chemical sense, giving As–C bond lengths of about 1.95 Å, and it gave better agreement with the $2kl$ intensities. This agreement was determined by assuming, after careful visual comparison, that $|F_o(2kl)| = |F_o(0kl)|$, except for a scale factor, and calculating R with $\Sigma|F_o| = \Sigma|F_c|$. In this way with $X_{As} = 0$, R for $(2kl)$ was 0.145 but with $X_{As(1)} = 1/4$ and $X_{As(2)} = 3/4$, R $(2kl)$ was 0.081.

Results and Description of the Structure. The agreement between observed and calculated structure factors is shown in Table 2 and the atomic co-ordinates are shown in Table 3. The more important interatomic distances and angles are shown in the Figure, which is a representation of the structure projected down a.

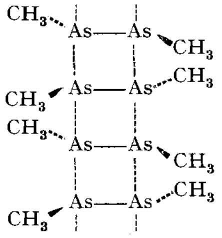
Table 2. *Observed and calculated structure factors for the Okl reflections*

h	k	e	$\vert 0 \vert F_o \vert$	$\vert 0 \vert F_c \vert$	h	k	e	$\vert 0 \vert F_o \vert$	$\vert 0 \vert F_c \vert$
0	0	2	2409	2328	0	3	5	590	588
0	0	4	1651	1689	0	3	7	433	445
0	0	6	1600	1519	0	3	9	254	297
0	0	8	960	934	0	3	11	191	175
0	0	10	504	550	0	3	13	106	97
0	0	12	342	356	0	3	15	68	50
0	0	14	222	186	0	4	0	378	379
0	0	16	115	74	0	4	2	294	282
0	1	1	651	648	0	4	4	191	221
0	1	3	478	513	0	4	6	191	234
0	1	5	385	399	0	4	8	156	145
0	1	7	275	299	0	4	10	73	71
0	1	9	181	193	0	4	12	69	64
0	1	11	104	111	0	4	14	76	32
0	1	13	22	61	0	5	1	369	354
0	1	15	64	32	0	5	3	319	315
0	2	0	1882	1728	0	5	5	282	256
0	2	2	1411	1340	0	5	7	192	194
0	2	4	1028	1033	0	5	9	147	133
0	2	6	925	956	0	5	11	142	79
0	2	8	607	624	0	6	0	19	8
0	2	10	327	348	0	6	2	19	24
0	2	12	227	236	0	6	4	19	24
0	2	14	161	123	0	6	6	20	8
0	2	16	86	45	0	6	8	21	13
0	3	1	889	850	0	7	1	93	66
0	3	3	723	728					

Table 3. *Final co-ordinates in fractions of the cell edge*

	x/a	y/b	z/c		x/a	y/b	z/c
As(1)	0.25	0.207	−0.013	C(1)	0.25	0.253	0.145
As(2)	0.75	0.207	−0.013	C(2)	0.75	0.213	−0.142

The arsenic atoms form a ladder structure parallel to *a* and these ladders lie in planes perpendicular to *c*. The shortest distance between two arsenic atoms in adjacent ladders is 3.4 Å. Within one ladder, depicted in **1**, the arsenic-arsenic rung distance of 2.4 Å is close to the normal single bond length found [6] in elementary As and in $(CH_3As)_5$ [2]. The inter-rung distance of 2.9 Å is shorter than the next nearest neighbour contacts in grey arsenic [6] (3.15 Å) and in skutterudite [7] (3.12 Å), and than the 1–3 cross ring contact (3.58 Å) in $(CH_3As)_5$ [2]. Each arsenic atom is also bonded to one carbon atom of a methyl group, average distance 1.97 Å, close to the value (1.95 Å) found in $(CH_3As)_5$ [2]. Along the ladder upright or on any one rung the methyl groups lie on opposite sides of the ladder. It seems reasonable to suggest that the long 2.9 Å arsenic-arsenic separation along the ladder upright corresponds to a one-electron bond with a bond order of close to 0.5. We then have trivalent arsenic



¦ denotes bond order 0.5

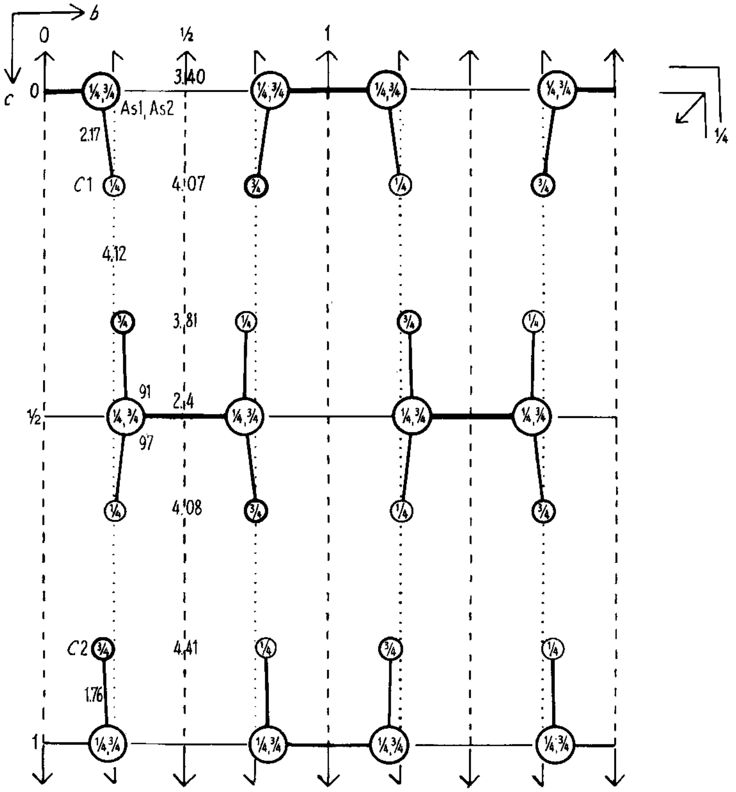
1

making one bond to a carbon atom and one to an arsenic atom on the same rung and two half bonds to the two arsenic atoms immediately above and below on the same upright.

The *van der Waals'* contacts between the carbon atoms of the methyl groups (Fig.) are close to 4 Å and show no unusual features.

The choice of space group may now be discussed in the light of the structure illustrated in the Figure; the present labelling of the axes is retained in this discussion and conventional space groups are given in parentheses. The space group *Imam* (No. 74 *Imma*) has mirror planes perpendicular to c at $z = 0, 1/2$ or at $z = 1/4, 3/4$ and we were unable to find a reasonable ordered structure in this space group. A random disordering of the methyl groups, with 'half' carbon atoms at the co-ordinates in Table 3 and two more 'half' carbon atoms with $x = 3/4$ and $1/4$ and the same y and z co-ordinates as in Table 3, would give short methyl...methyl contacts (close to 2.8 Å) in the space group *Imam* with mirror planes at $z = 0, 1/2$.

An examination of the Figure shows that the structure almost has centres of symmetry at 1/4, 0, 0 and at 0, 1/4, 1/4. If these were true centres, the space group would be *Imab* (No. 72 *Ibam*) but then the $hk0$ reflections would be absent for k odd;



The structure projected down the a *axis*

Estimated standard deviations As–As 0.02, As–C 0.1 Å. Distances in Å, angles in degrees and co-ordinates in fractions.

these reflections, though weak, are present. The contributions of the two arsenic atoms to the $hk0$ reflections cancel one another at present and the carbon atoms only contributy because they have different y co-ordinates. We suspect that the y (and possibly also the z) co-ordinates of the two arsenic atoms are not identical as shown in Table 3, but these two atoms could not be resolved in the $0kl$ projection.

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220. Aminofuroxane

1. Synthese und Struktur[1]

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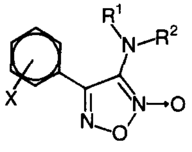
Summary. Phenylglyoximes are transformed in a single operation into 3-amino-4-phenylfuroxans which rearrange quantitatively to their 3-phenyl-4-amino-isomers above 80°. A mechanism for the synthesis is proposed and supported by the isolation of intermediates. Proof for the structure of both furoxan isomers and intermediate phenylaminoglyoximes rests on chemical transformations, mechanistic considerations, and the influence of certain structural changes on the UV.-spectra.

1. Einleitung. – Zur Untersuchung von pharmakologischen Struktur-Wirkungsbeziehungen wurden Aminofuroxane vom Typ **1** und **2** benötigt. In der vorliegenden Arbeit beschreiben wir eine einfache Synthese dieser Verbindungen und versuchen, ihre Struktur eindeutig festzulegen. Eine spätere Veröffentlichung wird sich mit thermischen und photochemischen Umlagerungen von Phenylaminofuroxanen befassen.



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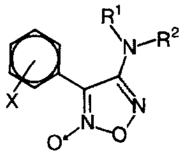

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[1] Teilweise vorgetragen am «2nd International Congress of Heterocyclic Chemistry», Montpellier, 11. Juli 1969.