The Crystal and Molecular Structure of 10-Halo-5, 10-dihydrophenarsazine*

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The 10-halo-5, 10-dihydrophenarsazine (phenarsazine halide) might be regarded as a tricyclic ring in which two benzene rings are connected by the arsenic and the nitrogen atoms. The present work was undertaken in order to elucidate the influence of the arsenic and the nitrogen atoms upon the configuration of this tricyclic ring. The disposition of halogen atoms around the arsenic atom would also be of interest in connection with the valence state of the arsenic atom. In the course of the present investigation, a paper on the structure of the chloride has already been published.1) It would be interesting to compare this result with ours, although ours is still in the stage of refinement.

Preliminary powder photographs seem to indicate that the crystals of the chloride, the bromide, and the iodide belong to the same crystal system, while the fluoride crystal belongs to a different system. Among these halides, the chloride, the bromide and the iodide gave needle crystals suitable for X-ray work. These crystals were found to be elongated along the *c* axes. Oscillation and Weissenberg photographs were prepared with Cu$K\alpha$ radiation. The crystal data are listed in Table I. The intensities were estimated visually with a calibrated scale by making use of the multiple-film technique. The corrections for polarization and Lorentz factors were applied in the usual way, and that for absorption was neglected.

The chloride was first studied. Since the *c* axis is shorter, the Patterson projection onto the (001) plane was computed, and it clearly revealed the interatomic vectors between arsenic and chlorine atoms as well as between arsenic atoms. The electron-density projection was then synthesized with the signs determined by the arsenic and chlorine atoms alone. Subsequent Fourier refinements made clear the positions of the lighter atoms. Electron-density projections along the other axes, obtained by means of the same procedure, gave the *z* coordinate of each atom. The reliability indices, *R*, were found to be 14.3, 17.7 and 22.4% for the *hk*0, *h*0*l* and 0*kl* spectra respectively. The isotropic temperature factors for all the atoms were estimated to be 3.2 Å^{-2} for the *hk*0 and 3.0 Å^{-2} for the *h*0*l* and 0*kl* spectra. Almost the same procedure of structure analysis was then applied to the bromide, the crystal structure of which was isomorphous with that of the chloride. The reliability index, *R*, was found to be 24.2, 22.1 and 36.3% for the *hk*0, *h*0*l* and 0*kl* spectra, the isotropic temperature factor being 5.0 Å^{-2} for the arsenic atom, 3.5 Å^{-2} for the bromine atom, and 5.0 Å^{-2} for the other atoms. The atomic coordinates in each crystal structure are listed in Table II.

TABLE I. CRYSTAL DATA

Phenarsazine chloride	Phenarsazine bromide
$C_{12}H_9AsClN$	$C_{12}H_9AsBrN$
Orthorhombic	Orthorhombic
$a=13.82$Å	$a=15.06$Å
$b=14.12$Å	$b=15.09$Å
$c=5.40$Å	$c=5.22$Å
$D_x=1.749$ g. cm^{-3} $(Z=4)$	$D_x=1.803$ g. cm^{-3} $(Z=4)$
$P2_12_12_1$	$P2_12_12_1$

Although the accuracy of analyses at this stage of refinement is not sufficient for us to discuss the results in detail, some interesting features of the molecular and crystal structure have been revealed. It may be remarked that the present results concerning the structure of the chloride agree approximately with those given by Camerman and Trotter,1) although our work was done independently with two-dimensional data. The general scheme of the crystal structure may be seen in Fig. 1, which shows the crystal structure of the bromide isomorphous with the chloride. The interatomic distances within a molecule as well as between nearest molecules were found to be plausible in comparison with conventional values. A molecule consists of two nearly equivalent halves related by a plane of symmetry through nitrogen, arsenic and bromine atoms. The tricyclic ring can be regarded as a plane, from which only the halogen atom deviates significantly. Thus, the nitrogen atom may be in the sp^2 state of hybridization, while the arsenic atom may be in the p^3 state, probably with a slight *d* character. This situation indicates the delocalization of the lone-pair electrons in these two atoms to the benzene rings; this is in conformity with the ultraviolet spectra results shown in Fig. 2. There may be no intermolecular forces other than those of the van der Waals type, which are seen in all the intermolecular distances.

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*) The major part of this paper was read at the symposium on Organometallic Compound, Nagoya, October, 1963, and also at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1964.

1) A. Camerman and J. Trotter, *J. Chem. Soc.*, **1965**, 730.

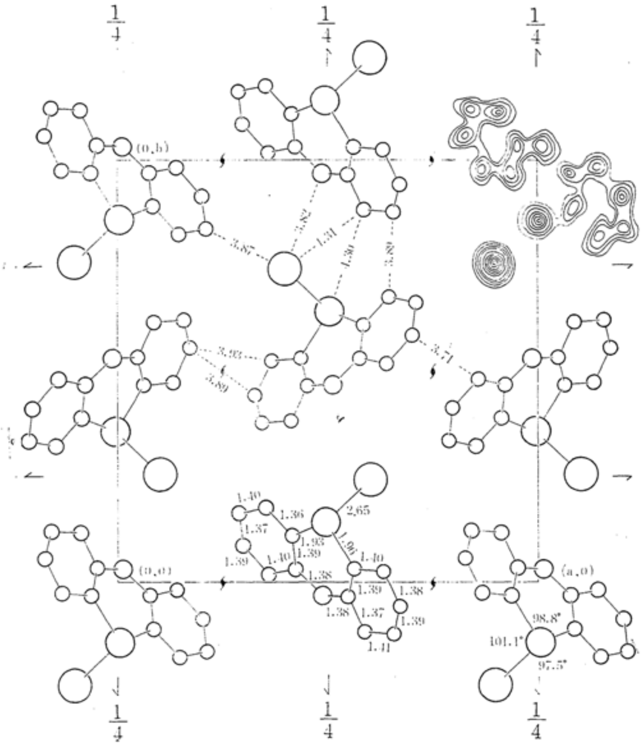

Fig. 1. Crystal structure and electron density projection of the bromide onto (001) plane, contours being at arbitrary scale.

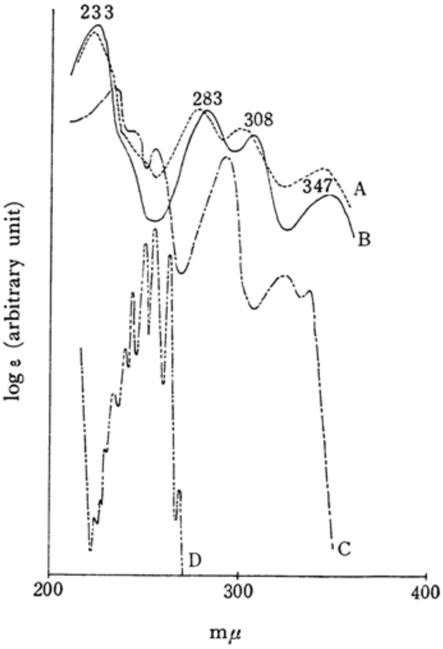

Fig. 2. Ultraviolet absorption spectra.

(A) Phenarsazine bromide
(B) Phenarsazine chloride
(C) Carbazole
(D) Benzene

TABLE II. ATOMIC PARAMETERS

Phenarsazine chloride				Phenarsazine bromide			
Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
C_1	0.549	0.049	0.142	C_1	0.563	0.032	0.193
C_2	0.619	0.038	0.300	C_2	0.633	0.025	0.367
C_3	0.687	−0.044	0.343	C_3	0.673	−0.057	0.361
C_4	0.653	−0.118	0.158	C_4	0.658	−0.123	0.180
C_5	0.604	−0.100	−0.008	C_5	0.587	−0.117	0.004
C_6	0.525	−0.017	−0.050	C_6	0.548	−0.035	0.012
C_7	0.407	0.053	−0.290	C_7	0.424	0.031	−0.238
C_8	0.350	0.037	−0.468	C_8	0.359	0.018	−0.425
C_9	0.269	0.098	−0.495	C_9	0.298	0.086	−0.468
C_{10}	0.271	0.177	−0.358	C_{10}	0.289	0.163	−0.333
C_{11}	0.325	0.187	−0.189	C_{11}	0.354	0.176	−0.146
C_{12}	0.401	0.133	−0.142	C_{12}	0.415	0.110	−0.103
N	0.477	−0.015	−0.233	N	0.488	−0.032	−0.188
Cl	0.583	0.249	−0.118	Br	0.603	0.243	−0.100
As	0.481	0.166	0.130	As	0.495	0.142	0.172

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