115. *Stereochemistry of Arsenic. Part XIII.*[1] 10-*Chloro-5,*10-*dihydrophenarsazine.*

By Arthur Camerman and James Trotter.

10-Chloro-5,10-dihydrophenarsazine crystallizes from xylene with half a molecule of xylene of crystallization, the crystals being monoclinic with $a = 14{\cdot}50$, $b = 16{\cdot}76$, $c = 13{\cdot}02$ Å, $\beta = 113{\cdot}7°$, space group Ia or $I2/a$, and having eight molecules of chlorodihydrophenarsazine and four molecules of xylene in the cell. This material rapidly loses the solvent of crystallization, the solvent-free crystals being orthorhombic, $a = 5{\cdot}47$, $b = 13{\cdot}91$, $c = 14{\cdot}30$ Å, $Z = 4$, space group $P2_12_12_1$. The complete structure of the orthorhombic crystals has been determined using scintillation counter data obtained with Cu-K_α radiation. The arsenic and chlorine positions were determined by Patterson methods, and the carbon and nitrogen atoms were located on a three-dimensional electron-density distribution. All the positional and anisotropic thermal parameters were then refined by five cycles of least squares, the final R factor being 0·056 for 1033 observed reflexions.

The molecule is slightly folded about the As–N axis, the angle between the two *o*-phenylene groups being 169°, and the chlorine atom being outside this angle (in addition one of the rings is slightly twisted as a result of intermolecular packing forces). The deviation from planarity is thus not very large and it is unlikely that geometrical isomers could be isolated. The most significant bond distances and valency angles are: As–Cl = 2·301 ± 0·004 Å, As–C = 1·917 ± 0·007 Å, C–N = 1·371 ± 0·009 Å, mean C–C = 1·406 ± 0·005 Å, ∠Cl–As–C = 96·1 ± 0·2°, ∠C–As–C = 97·0 ± 0·4°, ∠C–N–C = 128·0 ± 0·8°. The intermolecular separations correspond to van der Waals interactions.

If arsenic retains its usual valency angle (of about 98°) in a 5,10-disubstituted 5,10-dihydroarsanthren (I; R = alkyl or aryl), such a molecule must be folded about the As–As axis, the two *o*-phenylene groups subtending at this axis a (calculated) angle of 121°.[2] Three geometrical isomers should then exist: two *cis* forms, one having both substituents outside the 121° angle (steric factors permitting), and the other having both groups within this angle; and one *trans* form. Two forms of the 5,10-di-*p*-tolyl derivative (I; R = C_6H_4Me) have been isolated,[3] the third form being too sterically hindered to exist. It has recently been asserted however, on a theoretical basis, that systems such as (I) are unlikely to be

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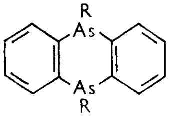
[1] Part XII, Cullen and Trotter, *Canad. J. Chem.*, 1963, **41**, 2983.

[2] Mann, *J.*, 1963, 4266.

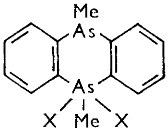
[3] Chatt and Mann, *J.*, 1940, 1184.

" stably folded " and that the existence of geometrical isomers is due to the stability of the arsenic pyramidal configuration.[4] The only direct structural information which appears to be available is that for 5,10-dihydro-5,10-dimethylarsanthren dibromide and di-iodide (II; X = Br or I), where the angle subtended by the *o*-phenylene groups was found to be, within rather wide limits of error, 157°.[5]

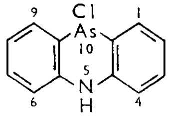
Recently it has been found that there appear to be two modifications of 10-chloro-5,10-dihydrophenarsazine (phenarsazine chloride, Adamsite, III); yellow crystals are obtained from a variety of solvents, and when these are heated to 200° at 10^{-3} mm. yellowish-green crystals are formed.[6] If the molecule is folded as in the dihydroarsanthren system two geometrical isomers might exist, one with the chlorine within and the other with the chlorine outside the angle formed by the two *o*-phenylene groups, the configuration at the nitrogen probably being readily inverted.



(I)



(II)



(III)

We have investigated the two crystalline modifications with *X*-rays to establish whether they are geometrical isomers, and to obtain details of the crystal and molecular structures. The results show that the yellow crystals are solvated, those from xylene containing one-half molecule of xylene per molecule of phenarsazine chloride. The yellowish-green crystals are solvent free, and a complete analysis shows that the *o*-phenylene groups subtend an angle of 169°, with the chlorine atom outside this angle; the deviation from complete planarity of the tricyclic ring system is thus quite small, and it is unlikely that geometrical isomers could be isolated.

Preliminary X-*Ray Study*.—10-Chloro-5,10-dihydrophenarsazine (phenarsazine chloride) is obtained, by reaction of diphenylamine and arsenic trichloride [7] and crystallization from any of a number of solvents (xylene, carbon tetrachloride, glacial acetic acid, etc.), as yellow single crystals which rapidly change to a yellow powder when removed from the mother-liquor. When either the single crystal sample or the powder is heated at $200°/10^{-3}$ mm., yellowish-green rectangular needles are formed, which are quite stable. Chemical analyses, infrared (solutions and potassium bromide discs) and ultraviolet spectra, and *X*-ray powder photographs of powdered yellow crystals, the yellow powder, and the green crystals (which are yellow when finely powdered) indicated that the three specimens are identical, so that the most reasonable explanation of the existence of two types of single crystals is that the yellow metastable modification contains solvent of crystallization, which is readily lost, and the stable green form is solvent free.

This conclusion was verified by determining the unit cell dimensions and space groups of the metastable yellow crystals (from xylene) and the stable green crystals, from various rotation, Weissenberg and precession photographs. The yellow crystals were sealed in thin-walled Lindemann-glass capillaries, together with some mother-liquor, to preserve them during the *X*-ray exposures. The densities were measured by flotation in carbon tetrachloride–methylcyclohexane for the yellow crystals, and in bromoform–chloroform for the green crystals.

Crystal data [$\lambda(\text{Cu-}K_\alpha) = 1{\cdot}5418$ Å; $\lambda(\text{Mo-}K_\alpha) = 0{\cdot}7107$ Å]. Metastable yellow crystals: Monoclinic, $a = 14{\cdot}50 \pm 0{\cdot}02$, $b = 16{\cdot}76 \pm 0{\cdot}02$, $c = 13{\cdot}02 \pm 0{\cdot}03$ Å, $\beta = 113{\cdot}7 \pm 0{\cdot}1°$; $U = 2898$ Å^3; $D_m = 1{\cdot}544$ g. cm.$^{-3}$; D_x $(Z = 8) = 1{\cdot}272$ g. cm.$^{-3}$; D_x $(Z = 8 + 4$

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[4] Mislow, Zimmerman, and Mellilo, *J. Amer. Chem. Soc.*, 1963, **85**, 594.

[5] Sutor and Harper, *Acta Cryst.*, 1959, **12**, 585.

[6] Cullen, personal communication.

[7] Burton and Gibson, *J.*, 1926, 451.

molecules of xylene) = 1·515 g. cm.$^{-3}$; Absent spectra: *hkl* when $h + k + l$ is odd, *h*0*l* when *h* or *l* is odd; space group is *Ia* or *I*2/*a*.

The density measurement indicates that the yellow crystals are solvated with half a molecule of xylene per molecule of phenarsazine chloride, $C_{12}H_9NAsCl,\frac{1}{2}C_8H_{10}$. Crystals from other solvents are no doubt also solvates.[8]

Stable yellowish-green crystals: Phenarsazine chloride, $C_{12}H_9NAsCl$, $M = 277·5$; Orthorhombic, $a = 5·47 \pm 0·01$, $b = 13·91 \pm 0·02$, $c = 14·30 \pm 0·02$ Å; $U = 1088$ Å^3; $D_m = 1·693$, $Z = 4$, $D_x = 1·694$ g. cm.$^{-3}$; Absorption coefficient for *X*-rays: $\lambda = 1·5418$ Å, $\mu = 66$ cm.$^{-1}$; $\lambda = 0·7107$ Å, $\mu = 35$ cm.$^{-1}$; $F(000) = 552$; absent spectra: *h*00 when *h* is odd, 0*k*0 when *k* is odd, 00*l* when *l* is odd; space group is $P2_12_12_1$.

The excellent agreement between measured and calculated densities indicates that the stable crystals are solvent-free.

STRUCTURE DETERMINATION OF STABLE CRYSTALS

Experimental.—Crystals of solvent-free phenarsazine chloride are stable yellowish-green needles elongated along *a*, with {011} developed. The intensities of all reflexions with $2\theta_{CuK_\alpha} \leqslant 148°$ (corresponding to a minimum interplanar spacing $d = 0·80$ Å) were measured on a G.E. XRD-5 Spectrogoniometer, with Single Crystal Orienter, using a scintillation counter, Cu-K_α radiation (nickel filter and pulse-height analyser), and the moving crystal–moving counter technique.[9] The crystal was mounted with *a* parallel to the ϕ axis of the goniostat, and had cross-section about 0·3 × 0·3 mm., so that absorption corrections were not considered necessary. The structure amplitudes were derived as usual. 1033 reflexions were observed, 79% of the total number in the range $0 < 2\theta_{CuK_\alpha} \leqslant 148°$.

Structure Analysis.—The *y*- and *z*-co-ordinates of the arsenic and chlorine atoms were determined from the 0*kl* Patterson function and an 0*kl* Fourier series was summed with phases based on the As and Cl atoms. On the resulting electron-density distribution all the atoms (except hydrogens) were readily discernible. Structure factors were calculated from the positions obtained from the Fourier map and *R* for the zone was 0·135.

The *x*-co-ordinates of the arsenic and chlorine atoms were then determined from the *h*0*l* Patterson function and an *h*0*l* Fourier series was summed with phases based on the arsenic and chlorine atoms. There was much overlap in the resulting electron-density distribution so that the *x*-co-ordinates of the rest of the atoms could not be obtained with certainty. A three-dimensional Fourier series was then summed based on the phases of the arsenic and chlorine atoms only and from the resulting electron-density distribution the *x*-co-ordinates of all the atoms could be obtained.

Structure amplitudes, calculated with the positions obtained from the electron-density map, gave $R = 0·133$ for all the observed *hkl* reflexions. Throughout this structure determination the scattering factors of the International Tables[10] were used, with initially $B = 4·5$ Å^2 for all the atoms except arsenic, for which $B = 3·0$ Å^2 was used.

Refinement of the positional and anisotropic thermal parameters for all atoms except hydrogens then proceeded by (block diagonal) least-squares. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $\sqrt{w} = |F_o|/35$ when $|F_o| < 35$; and $\sqrt{w} = 35/|F_o|$ when $|F_o| \geqslant 35$. Refinement was complete in five cycles during which *R* was reduced from 0·133 to 0·056, and $\Sigma w\Delta F^2$ from $6·2 \times 10^3$ to $1·7 \times 10^3$.

The measured structure amplitudes are compared in Table 1 with the values calculated from the final parameters, those from the fifth least squares cycles ($R = 0·056$ for the 1033 observed reflexions).

Atomic parameters and molecular dimensions. The final positional and thermal parameters are given in Table 2 (the numbering of the atoms used in Table 2 and throughout the remainder of this Paper is for convenience in the crystallographic analysis, and is illustrated in Fig. 1); *x*, *y*, and *z* are fractional co-ordinates referred to the crystal axes, and b_{ij} are the anisotropic thermal parameters in the expression:

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

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[8] Jackson, *Chem. Rev.*, 1935, **17**, 251.

[9] Furnas, "Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee, 1957.

[10] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, 1962, Vol. III.

TABLE 1.

Measured and calculated structure amplitudes. (Unobserved reflexions, which are listed as 0·0, have threshold values in the range 2—9).

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
0	0	2	6·8	0·3	0	5	13	11·3	9·9	0	11	7	21·3	22·7	1	1	13	16·5	16·1	1	6	14	20·2	20·8
0	0	4	8·8	3·0	0	5	14	22·2	21·5	0	11	8	0·0	9·3	1	1	14	9·5	7·0	1	6	15	10·9	11·5
0	0	6	60·1	63·5	0	5	15	17·4	18·7	0	11	9	24·3	24·3	1	1	15	19·5	19·2	1	6	16	8·4	9·9
0	0	8	11·8	8·9	0	5	16	12·0	14·1	0	11	10	0·0	2·4	1	1	16	16·5	17·2	1	7	0	58·1	59·5
0	0	10	54·7	53·6	0	5	17	7·2	7·2	0	11	11	9·9	11·0	1	1	17	7·2	9·6	1	7	1	30·6	31·7
0	0	12	43·1	42·5	0	6	0	22·7	22·5	0	11	12	0·0	6·2	1	2	0	44·9	44·8	1	7	2	41·3	43·1
0	0	14	44·7	46·5	0	6	1	51·7	49·6	0	11	13	8·1	9·1	1	2	1	108·3	121·4	1	7	3	53·6	55·5
0	0	16	0·0	7·0	0	6	2	16·3	14·7	0	12	0	29·3	28·6	1	2	2	98·1	97·8	1	7	4	43·8	45·1
0	1	1	13·1	13·4	0	6	3	13·6	13·1	0	12	1	33·8	33·4	1	2	3	33·8	31·1	1	7	5	33·1	33·5
0	1	2	107·4	126·4	0	6	4	35·2	38·0	0	12	2	23·3	22·7	1	2	4	68·5	64·5	1	7	6	13·1	14·0
0	1	3	54·9	55·4	0	6	5	36·1	34·5	0	12	3	0·0	4·1	1	2	5	49·2	46·6	1	7	7	41·5	40·3
0	1	4	86·3	88·4	0	6	6	89·4	89·2	0	12	4	0·0	2·8	1	2	6	52·2	50·5	1	7	8	16·5	14·5
0	1	5	25·2	22·5	0	6	7	40·4	37·2	0	12	5	31·3	31·5	1	2	7	24·5	24·3	1	7	9	19·3	17·3
0	1	6	19·9	20·0	0	6	8	38·8	38·4	0	12	6	0·0	8·3	1	2	8	64·0	62·2	1	7	10	29·0	28·5
0	1	7	0·0	7·5	0	6	9	0·0	4·6	0	12	7	25·6	26·1	1	2	9	0·0	3·6	1	7	11	15·9	15·7
0	1	8	68·5	68·8	0	6	10	0·0	0·1	0	12	8	0·0	5·9	1	2	10	29·0	29·4	1	7	12	19·5	19·0
0	1	9	16·1	16·9	0	6	11	23·3	20·7	0	12	9	0·0	3·0	1	2	11	39·9	41·0	1	7	13	14·5	14·5
0	1	10	54·0	53·7	0	6	12	14·9	11·3	0	12	10	11·3	12·0	1	2	12	10·6	9·2	1	7	14	21·1	20·6
0	1	11	12·7	13·7	0	6	13	24·9	22·5	0	12	11	17·7	20·2	1	2	13	29·7	30·6	1	7	15	8·6	10·0
0	1	12	23·6	24·0	0	6	14	0·0	1·2	0	12	12	9·0	9·7	1	2	14	23·1	24·9	1	7	16	6·5	8·3
0	1	13	0·0	0·2	0	6	15	0·0	1·3	0	13	1	24·3	23·5	1	2	15	10·6	11·0	1	8	0	43·8	46·6
0	1	14	16·8	17·2	0	6	16	16·5	17·2	0	13	2	0·0	1·3	1	2	16	13·1	12·5	1	8	1	12·7	12·3
0	1	15	0·0	1·6	0	7	1	8·1	6·5	0	13	3	28·6	27·3	1	2	17	13·4	13·0	1	8	2	48·3	48·3
0	1	16	27·9	29·4	0	7	2	32·2	30·5	0	13	4	0·0	4·1	1	3	0	43·1	47·9	1	8	3	36·3	38·1
0	1	17	0·0	0·6	0	7	3	47·9	48·5	0	13	5	17·4	18·1	1	3	1	88·5	89·1	1	8	4	18·4	18·0
0	2	0	121·7	146·9	0	7	4	44·0	43·5	0	13	6	0·0	1·3	1	3	2	94·7	98·6	1	8	5	33·6	34·4
0	2	1	35·2	33·9	0	7	5	39·5	38·3	0	13	7	15·2	16·3	1	3	3	69·2	68·5	1	8	6	9·5	8·2
0	2	2	21·3	24·8	0	7	6	0·0	1·7	0	13	8	0·0	5·3	1	3	4	47·6	45·9	1	8	7	22·7	21·3
0	2	3	95·3	100·0	0	7	7	14·0	12·5	0	13	9	29·9	31·4	1	3	5	44·7	44·0	1	8	8	20·2	20·5
0	2	4	12·7	13·0	0	7	8	35·4	34·8	0	13	10	0·0	0·3	1	3	6	53·8	53·7	1	8	9	34·7	34·0
0	2	5	65·8	61·7	0	7	9	22·2	20·7	0	13	11	7·2	9·2	1	3	7	26·1	24·8	1	8	10	16·5	14·0
0	2	6	74·7	73·5	0	7	10	25·4	24·0	0	14	0	13·1	14·4	1	3	8	36·3	34·9	1	8	11	10·9	10·6
0	2	7	38·6	37·2	0	7	11	17·2	17·4	0	14	1	18·1	18·4	1	3	9	47·6	48·4	1	8	12	28·6	29·0
0	2	8	0·0	3·9	0	7	12	0·0	2·9	0	14	2	0·0	6·0	1	3	10	24·5	24·2	1	8	13	0·0	6·8
0	2	9	18·8	17·5	0	7	13	17·0	17·3	0	14	3	23·1	23·5	1	3	11	22·7	22·1	1	8	14	14·9	16·1
0	2	10	45·6	46·8	0	7	14	18·1	17·5	0	14	4	0·0	3·4	1	3	12	31·5	31·8	1	8	15	9·7	9·5
0	2	11	17·7	20·0	0	7	15	19·3	20·9	0	14	5	23·3	23·7	1	3	13	26·3	27·1	1	9	0	0·0	3·4
0	2	12	48·3	48·9	0	7	16	7·7	9·3	0	14	6	0·0	8·6	1	3	14	0·0	10·1	1	9	1	18·8	18·6
0	2	13	0·0	3·4	0	8	0	32·0	32·2	0	14	7	25·6	26·3	1	3	15	21·1	22·1	1	9	2	22·0	21·6
0	2	14	13·4	13·7	0	8	1	63·1	61·9	0	14	8	0·0	4·7	1	3	16	8·1	8·5	1	9	3	28·1	28·7
0	2	15	0·0	2·2	0	8	2	0·0	10·2	0	14	9	0·0	5·7	1	3	17	0·0	4·2	1	9	4	22·1	23·3
0	2	16	9·5	9·7	0	8	3	37·9	35·1	0	14	10	0·0	3·6	1	4	0	22·7	17·1	1	9	5	37·7	37·6
0	2	17	10·6	12·0	0	8	4	40·2	38·6	0	15	1	18·6	20·9	1	4	1	25·1	24·7	1	9	6	23·3	22·0
0	3	1	20·8	18·3	0	8	5	13·6	14·0	0	15	2	0·0	5·5	1	4	2	71·3	72·0	1	9	7	34·2	34·9
0	3	2	71·3	75·7	0	8	6	44·7	44·2	0	15	3	0·0	5·0	1	4	3	59·2	57·4	1	9	8	24·7	24·0
0	3	3	13·4	16·8	0	8	7	24·0	27·7	0	15	4	0·0	6·4	1	4	4	59·2	59·1	1	9	9	23·8	11·7
0	3	4	71·5	71·1	0	8	8	12·2	11·1	0	15	5	10·2	10·9	1	4	5	41·5	42·9	1	9	10	13·1	13·5
0	3	5	17·4	15·0	0	8	9	20·6	19·6	0	15	6	0·0	0·2	1	4	6	40·6	37·4	1	9	11	0·0	4·6
0	3	6	32·2	32·4	0	8	10	0·0	4·7	0	15	7	7·2	8·6	1	4	7	49·5	48·0	1	9	12	12·7	13·8
0	3	7	30·8	30·1	0	8	11	34·0	33·4	0	15	8	0·0	2·8	1	4	8	39·7	39·4	1	9	13	0·0	9·3
0	3	8	41·3	41·1	0	8	12	15·2	17·1	0	16	0	14·9	13·7	1	4	9	14·9	12·7	1	9	14	11·5	11·7
0	3	9	27·9	26·1	0	8	13	27·2	27·4	0	16	1	0·0	4·4	1	4	10	13·6	12·1	1	9	15	9·3	10·1
0	3	10	51·5	52·6	0	8	14	0·0	1·1	0	16	2	0·0	1·1	1	4	11	21·8	20·4	1	10	0	35·6	35·7
0	3	11	0·0	1·2	0	8	15	0·0	6·0	0	16	3	0·0	1·6	1	4	12	0·0	5·2	1	10	1	30·6	31·3
0	3	12	11·5	10·1	0	9	1	29·9	28·4	0	16	4	0·0	2·6	1	4	13	0·0	12·3	1	10	2	27·2	27·2
0	3	13	10·2	8·1	0	9	2	43·3	41·3	0	16	5	14·9	16·7	1	4	14	17·9	20·6	1	10	3	35·2	36·4
0	3	14	21·1	20·7	0	9	3	49·2	49·0	0	16	6	0·0	3·1	1	4	15	11·3	12·0	1	10	4	13·8	14·8
0	3	15	0·0	2·8	0	9	4	17·0	18·4	0	17	1	7·4	10·1	1	4	16	12·4	14·1	1	10	5	13·8	12·4
0	3	16	24·7	25·4	0	9	5	22·2	21·0	0	17	2	0·0	1·0	1	4	17	15·9	17·3	1	10	6	17·9	16·5
0	3	17	0·0	0·4	0	9	6	0·0	4·5	0	17	3	12·9	13·3	1	5	0	77·2	80·5	1	10	7	12·2	11·2
0	4	0	43·1	43·2	0	9	7	22·7	22·3	1	0	1	84·7	87·9	1	5	1	32·9	32·8	1	10	8	12·2	10·9
0	4	1	32·9	27·7	0	9	8	17·0	16·6	1	0	2	25·4	24·6	1	5	2	47·2	47·1	1	10	9	27·4	26·1
0	4	2	34·5	34·1	0	9	9	27·7	24·7	1	0	3	84·7	77·9	1	5	3	38·8	41·7	1	10	10	22·4	22·9
0	4	3	24·3	23·6	0	9	10	0·0	2·4	1	0	4	26·5	30·3	1	5	4	28·3	28·5	1	10	11	10·4	9·6
0	4	4	47·6	48·8	0	9	11	16·5	16·4	1	0	5	33·8	37·0	1	5	5	46·5	45·2	1	10	12	18·4	18·7
0	4	5	84·7	78·7	0	9	12	0·0	5·5	1	0	6	0·0	4·3	1	5	6	19·3	17·2	1	10	13	10·6	10·0
0	4	6	104·2	105·2	0	9	13	15·2	15·5	1	0	7	25·6	25·5	1	5	7	25·4	24·6	1	10	14	10·9	11·7
0	4	7	32·2	33·3	0	9	14	12·2	13·4	1	0	8	55·6	57·0	1	5	8	27·9	27·3	1	11	0	15·4	11·9
0	4	8	41·5	40·2	0	9	15	21·3	22·2	1	0	9	18·1	15·6	1	5	9	39·5	39·9	1	11	1	20·2	20·2
0	4	9	16·5	16·5	0	10	0	30·6	29·3	1	0	10	29·7	31·3	1	5	10	36·7	36·2	1	11	2	31·1	32·2
0	4	10	0·0	2·1	0	10	1	50·4	50·8	1	0	11	53·6	56·0	1	5	11	23·1	21·7	1	11	3	21·3	21·8
0	4	11	0·0	7·6	0	10	2	30·6	28·5	1	0	12	0·0	2·5	1	5	12	26·5	25·0	1	11	4	20·6	21·3
0	4	12	44·9	45·5	0	10	3	21·3	20·0	1	0	13	13·8	15·8	1	5	13	21·1	19·6	1	11	5	29·3	24·9
0	4	13	0·0	2·1	0	10	4	0·0	6·2	1	0	14	27·9	29·6	1	5	14	17·7	17·4	1	11	6	20·4	18·1
0	4	14	0·0	3·3	0	10	5	32·7	32·5	1	0	15	9·3	8·7	1	5	15	11·1	11·0	1	11	7	28·3	27·5
0	4	15	14·7	13·1	0	10	6	0·0	1·3	1	0	16	0·0	6·9	1	5	16	0·0	5·7	1	11	8	25·6	24·4
0	4	16	14·5	16·5	0	10	7	0·0	3·2	1	0	17	0·0	1·9	1	6	0	17·7	17·0	1	11	9	0·0	2·9
0	4	17	11·3	13·2	0	10	8	0·0	4·8	1	1	0	25·8	29·7	1	6	1	26·3	29·2	1	11	10	14·3	14·0
0	5	1	37·9	36·7	0	10	9	10·6	6·5	1	1	1	66·3	71·6	1	6	2	46·3	47·8	1	11	11	14·0	13·1
0	5	2	51·7	55·3	0	10	10	13·6	12·7	1	1	2	12·2	13·8	1	6	3	44·7	45·3	1	11	12	0·0	4·8
0	5	3	66·3	63·9	0	10	11	34·5	35·6	1	1	3	88·5	83·2	1	6	4	39·2	41·1	1	11	13	11·5	13·3
0	5	4	86·0	85·5	0	10	12	13·6	13·3	1	1	4	80·1	79·2	1	6	5	55·1	55·6	1	12	0	34·5	35·4
0	5	5	8·6	11·3	0	10	13	23·8	23·5	1	1	5	26·5	24·9	1	6	6	25·4	24·8	1	12	1	12·2	12·4
0	5	6	26·1	24·4	0	10	14	0·0	3·0	1	1	6	65·4	64·9	1	6	7	44·9	44·8	1	12	2	11·3	9·1
0	5	7	20·8	22·5	0	11	1	23·1	21·9	1	1	7	45·1	42·4	1	6	8	34·2	34·2	1	12	3	28·6	29·6
0	5	8	23·1	21·8	0	11	2	0·0	7·0	1	1	8	46·5	47·2	1	6	9	34·7	34·6	1	12	4	17·9	16·1
0	5	9	19·3	19·4	0	11	3	37·9	38·0	1	1	9	30·2	32·3	1	6	10	19·0	18·1	1	12	5	12·7	12·5
0	5	10	55·6	55·7	0	11	4	20·2	22·2	1	1	10	16·3	17·3	1	6	11	0·0	8·1	1	12	6	25·8	24·3
0	5	11	19·0	18·2	0	11	5	12·2	10·9	1	1	11	19·0	18·8	1	6	12	17·9	18·1	1	12	7	0·0	7·4
0	5	12	0·0	9·0	0	11	6	0·0	5·5	1	1	12	19·7	19·5	1	6	13	9·5	13·4	1	12	8	9·3	10·6

TABLE 1. (*Continued.*)

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c
1	12	9	17·4	18·4	2	2	8	0·0	6·6	2	7	14	0·0	0·2	2	14	8	13·4	14·8	3	4	11	18·1	18·1
1	12	10	9·7	9·9	2	2	9	58·1	58·1	2	7	15	0·0	1·6	2	14	9	0·0	4·9	3	4	12	9·3	10·6
1	12	11	7·4	8·2	2	2	10	0·0	6·3	2	7	0	0·0	1·6	2	15	0	25·8	25·9	3	4	13	9·5	10·5
1	12	12	7·9	8·0	2	2	11	19·7	18·5	2	8	1	14·3	14·6	2	15	1	0·0	1·8	3	4	14	10·6	9·6
1	13	0	10·6	3·2	2	2	12	0·0	2·0	2	8	2	39·2	40·4	2	15	2	16·3	18·4	3	4	15	7·2	8·2
1	13	1	21·8	23·4	2	2	13	17·4	16·4	2	8	3	39·9	38·5	2	15	3	0·0	1·9	3	5	0	51·7	52·3
1	13	2	21·1	19·9	2	2	14	12·4	13·6	2	8	4	35·8	35·8	2	15	4	0·0	3·9	3	5	1	38·3	37·9
1	13	3	0·0	3·8	2	2	15	20·6	22·5	2	8	5	28·6	29·8	2	15	5	0·0	0·8	3	5	2	29·7	29·8
1	13	4	15·9	17·6	2	2	16	9·3	10·1	2	8	6	17·9	17·9	2	15	6	7·7	9·0	3	5	3	34·5	36·0
1	13	5	0·0	6·4	2	3	0	53·1	52·1	2	8	7	23·3	23·5	2	15	7	7·7	8·0	3	5	4	24·3	24·3
1	13	6	10·4	9·8	2	3	1	94·9	96·4	2	8	6	28·1	25·1	2	16	0	0·0	1·2	3	5	5	13·4	14·3
1	13	7	11·1	10·5	2	3	2	42·2	42·0	2	8	9	27·2	27·5	2	16	1	6·3	3·0	3	5	6	25·4	23·9
1	13	8	11·5	11·1	2	3	3	9·7	10·8	3	8	10	21·3	21·0	2	16	2	15·6	16·4	3	5	7	13·6	13·0
1	13	9	7·9	9·9	2	3	4	33·6	31·7	2	8	11	16·8	17·4	2	16	3	0·0	2·5	3	5	8	10·9	8·2
1	13	10	13·8	14·9	2	3	5	66·3	65·1	2	8	12	0·0	5·5	2	16	4	9·0	9·6	3	5	9	28·6	25·7
1	13	11	12·2	11·1	2	3	6	11·5	9·9	2	8	13	0·0	7·1	3	0	1	79·2	77·6	3	5	10	20·8	21·3
1	14	0	0·0	4·6	2	3	7	47·6	48·4	2	8	14	10·4	11·5	3	0	2	40·8	39·7	3	5	11	19·7	20·0
1	14	1	10·2	6·2	2	3	8	10·9	12·4	2	9	0	30·4	30·2	3	0	3	0·0	3·1	3	5	12	23·8	22·7
1	14	2	0·0	5·9	2	3	9	0·0	4·2	2	9	1	16·1	16·3	3	0	4	26·1	24·1	3	5	13	8·1	9·3
1	14	3	18·1	20·8	2	3	10	19·9	18·9	2	9	2	10·2	9·6	3	0	5	21·5	22·1	3	5	14	13·8	15·4
1	14	4	10·4	10·8	2	3	11	28·6	29·9	2	9	3	8·8	9·1	3	0	6	0·0	5·4	3	5	15	12·4	14·1
1	14	5	8·6	8·9	2	3	12	26·1	25·6	2	9	4	37·0	36·7	3	0	7	25·4	24·5	3	6	0	29·3	28·2
1	14	6	21·8	23·3	2	3	13	27·0	24·8	2	9	5	33·1	33·6	3	0	8	18·1	18·8	3	6	1	24·7	24·0
1	14	7	0·0	4·3	2	3	14	15·2	15·8	2	9	6	56·3	55·8	3	0	9	11·5	12·9	3	6	2	27·9	27·8
1	14	8	12·2	12·5	2	3	15	0·0	2·0	2	9	7	14·5	14·4	3	0	10	28·3	29·3	3	6	3	17·0	15·8
1	14	9	11·8	12·2	2	3	16	0·0	4·4	2	9	8	30·4	30·3	3	0	11	27·4	28·3	3	6	4	35·4	36·3
1	14	10	0·0	3·8	2	4	0	5·6	0·0	2	9	9	11·3	9·9	3	0	12	0·0	2·0	3	6	5	31·5	29·9
1	15	0	9·3	3·5	2	4	1	52·4	49·1	2	9	10	0·0	0·2	3	0	13	18·6	21·2	3	6	6	27·9	25·9
1	15	1	23·8	23·7	2	4	2	21·5	23·9	2	9	11	10·9	13·1	3	0	14	0·0	9·7	3	6	7	55·1	53·5
1	15	2	10·9	10·9	2	4	3	79·4	82·7	2	9	12	12·4	13·1	3	0	15	0·0	1·4	3	6	8	12·0	12·3
1	15	3	0·0	4·8	2	4	4	39·7	38·0	2	9	13	15·4	15·2	3	0	16	13·6	16·4	3	6	9	0·0	8·0
1	15	4	12·2	13·1	2	4	5	37·4	37·1	2	9	14	0·0	3·8	3	1	0	34·9	34·6	3	6	10	18·4	18·5
1	15	5	0·0	8·6	2	4	6	17·4	16·7	2	10	0	8·4	10·1	3	1	1	27·7	29·4	3	6	11	18·4	18·0
1	15	6	0·0	2·9	2	4	7	27·4	26·4	2	10	1	0·0	6·0	3	1	2	18·8	17·0	3	6	12	19·0	18·3
1	15	7	7·2	8·5	2	4	8	20·2	19·7	2	10	2	34·2	36·3	3	1	3	69·7	65·3	3	6	13	0·0	5·2
1	15	8	8·1	7·7	2	4	9	49·9	48·6	2	10	3	9·7	9·4	3	1	4	24·0	23·1	3	6	14	9·3	8·6
1	16	0	11·3	10·0	2	4	10	19·9	19·0	2	10	4	31·7	30·9	3	1	5	25·2	25·6	3	7	0	30·8	30·0
1	16	1	11·5	9·7	2	4	11	17·7	15·2	2	10	5	14·5	12·6	3	1	6	51·5	50·5	3	7	1	19·7	19·7
1	16	2	0·0	1·3	2	4	12	0·0	4·8	2	10	6	13·4	11·7	3	1	7	23·8	22·4	3	7	2	36·1	36·6
1	16	3	15·6	15·8	2	4	13	17·2	17·7	2	10	7	12·7	11·2	3	1	8	34·2	34·3	3	7	3	24·7	24·2
1	16	4	11·5	12·3	2	4	14	12·0	13·7	2	10	8	30·4	29·4	3	1	9	31·7	31·9	3	7	4	37·9	39·0
1	16	5	0·0	3·7	2	4	15	20·6	23·0	2	10	9	10·9	13·6	3	1	10	10·4	5·0	3	7	5	37·2	36·0
1	16	6	11·1	12·2	2	4	16	6·8	7·8	2	10	10	22·2	21·9	3	1	11	0·0	9·4	3	7	6	17·7	14·8
1	17	0	7·0	4·8	2	5	0	52·6	52·6	2	10	11	13·6	12·6	3	1	12	18·8	15·5	3	7	7	24·5	21·8
1	17	1	8·4	8·9	2	5	1	85·8	87·9	2	10	12	0·0	4·0	3	1	13	17·0	16·9	3	7	8	12·0	6·0
1	17	2	7·4	8·5	2	5	2	59·7	59·0	2	10	13	6·8	6·8	3	1	14	0·0	3·7	3	7	9	19·7	19·0
2	0	0	8·6	13·7	2	5	3	22·9	24·0	2	11	0	27·9	26·7	3	1	15	15·2	16·7	3	7	10	21·8	22·4
2	0	1	27·2	28·4	2	5	4	34·0	33·5	2	11	1	14·7	14·3	3	2	0	31·3	31·0	3	7	11	9·5	9·4
2	0	2	0·0	3·5	2	5	5	25·8	25·7	2	11	2	10·9	10·8	3	2	1	53·6	54·4	3	7	12	19·3	19·8
2	0	3	98·5	94·3	2	5	6	32·2	32·0	2	11	3	15·2	14·4	3	2	2	45·6	45·1	3	7	13	0·0	6·3
2	0	4	7·2	10·3	2	5	7	28·3	27·9	2	11	4	19·0	19·2	3	2	3	0·0	4·9	3	7	14	12·9	13·5
2	0	5	26·8	25·7	2	5	8	0·0	3·6	2	11	5	21·3	17·9	3	2	4	35·6	35·1	3	7	0	35·6	36·8
2	0	6	23·3	20·8	2	5	9	30·4	30·0	2	11	6	29·5	28·1	3	2	5	41·7	41·6	3	8	1	12·9	13·3
2	0	7	29·9	31·8	2	5	10	11·3	11·9	2	11	7	15·9	15·5	3	2	6	29·3	28·4	3	8	2	18·5	18·7
2	0	8	11·8	10·3	2	5	11	37·7	38·7	2	11	8	17·2	18·4	3	2	7	26·3	27·0	3	8	3	20·6	21·0
2	0	9	65·1	66·0	2	5	12	29·9	28·9	2	11	9	0·0	7·0	3	2	8	32·9	32·1	3	8	4	22·9	20·2
2	0	10	10·4	11·1	2	5	13	26·8	27·3	2	11	10	7·9	7·8	3	2	9	12·9	11·6	3	8	5	30·8	31·1
2	0	11	24·9	27·3	2	5	14	10·2	11·1	2	11	11	0·0	0·2	3	2	10	24·0	25·5	3	8	6	27·9	26·3
2	0	12	0·0	2·7	2	5	15	0·0	4·3	2	11	12	12·9	13·9	3	2	11	29·7	31·2	3	8	7	18·1	16·5
2	0	13	16·8	18·8	2	5	16	0·0	5·1	2	12	0	0·0	1·7	3	2	12	0·0	4·5	3	8	8	11·8	11·8
2	0	14	0·0	6·5	2	6	0	17·0	16·2	2	12	1	0·0	7·5	3	2	13	18·6	18·3	3	8	9	0·0	7·9
2	0	15	22·7	24·8	2	6	1	23·8	23·1	2	12	2	22·7	23·3	3	2	14	9·3	10·3	3	8	10	27·2	24·6
2	0	16	0·0	1·4	2	6	2	28·6	29·1	2	12	3	9·9	8·3	3	2	15	0·0	5·0	3	8	11	16·3	14·2
2	0	17	10·4	11·3	2	6	3	54·7	54·3	2	12	4	21·1	20·2	3	3	0	50·8	51·2	3	8	12	16·8	17·7
2	1	0	34·9	35·0	2	6	4	46·1	47·3	2	12	5	0·0	3·2	3	3	1	34·9	35·2	3	8	13	7·0	7·2
2	1	1	35·2	39·7	2	6	5	11·3	8·5	2	12	6	0·0	5·8	3	3	2	14·9	16·4	3	9	0	16·5	16·0
2	1	2	20·6	20·3	2	6	6	21·8	21·9	2	12	7	8·8	8·8	3	3	3	40·4	39·5	3	9	1	0·0	5·1
2	1	3	43·1	40·1	2	6	7	24·9	26·1	2	12	8	18·1	17·1	3	3	4	30·8	29·1	3	9	2	23·8	25·5
2	1	4	36·1	33·7	2	6	8	28·3	27·3	2	12	9	0·0	4·5	3	3	5	22·2	20·5	3	9	3	18·1	16·9
2	1	5	72·6	70·4	2	6	9	19·5	17·0	2	12	10	13·6	14·3	3	3	6	36·5	35·9	3	9	4	13·4	12·3
2	1	6	0·0	4·4	2	6	10	27·7	26·2	2	12	11	0·0	4·6	3	3	7	21·8	18·7	3	9	5	32·4	31·8
2	1	7	93·3	91·3	2	6	11	0·0	8·0	2	12	0	35·4	36·1	3	3	8	26·5	27·2	3	9	6	13·1	12·6
2	1	8	0·0	2·7	2	6	12	0·0	6·8	2	13	1	0·0	8·3	3	3	9	41·7	39·9	3	9	7	18·8	17·3
2	1	9	11·1	12·5	2	6	13	16·1	16·0	2	13	2	15·4	18·4	3	3	10	16·1	16·2	3	9	8	13·6	14·7
2	1	10	21·1	19·9	2	6	14	12·9	13·5	2	13	3	0·0	6·9	3	3	11	18·8	22·0	3	9	9	13·1	13·7
2	1	11	27·7	28·2	2	6	15	16·5	17·7	2	13	4	0·0	5·1	3	3	12	17·0	18·4	3	9	10	0·0	9·0
2	1	12	16·3	15·4	2	7	0	16·8	18·6	2	13	5	12·2	11·6	3	3	13	16·8	17·9	3	9	11	0·0	5·5
2	1	13	19·7	21·0	2	7	1	53·6	53·2	2	13	6	16·5	16·0	3	3	14	7·9	8·5	3	9	12	9·5	10·3
2	1	14	0·0	10·5	2	7	2	0·0	6·3	2	13	7	11·3	10·5	3	3	15	16·8	18·5	3	9	13	9·3	11·0
2	1	15	10·6	10·7	2	7	3	23·8	23·7	2	13	8	10·2	10.0	3	4	0	0·0	5·1	3	10	0	35·4	36·2
2	1	16	0·0	6·3	2	7	4	36·5	35·9	2	13	9	0·0	4·5	3	4	1	29·7	30·6	3	10	1	22·7	24·9
2	1	17	22·0	25·2	2	7	5	24·5	25·4	2	13	10	16·3	16·5	3	4	2	30·4	32·3	3	10	2	12·2	12·1
2	2	0	19·3	15·2	2	7	6	44·7	45·4	2	14	0	8·4	5·0	3	4	3	14·0	14·9	3	10	3	15·2	16·1
2	2	1	43·8	44·0	2	7	7	18·6	15·0	2	14	1	0·0	6·0	3	4	4	42·2	41·8	3	10	4	14·0	12·3
2	2	2	20·2	18·9	2	7	8	14·5	12·6	2	14	2	22·9	22·8	3	4	5	38·1	36·7	3	10	5	23·1	21·5
2	2	3	71·7	74·7	2	7	9	17·2	12·8	2	14	3	0·0	1·3	3	4	6	30·2	28·6	3	10	6	14·9	15·7
2	2	4	10·4	12·4	2	7	10	12·9	11·5	2	14	4	17·7	19·2	3	4	7	33·6	31·1	3	10	7	9·0	10·0
2	2	5	32·0	32·2	2	7	11	29·7	28·6	2	14	5	0·0	2·4	3	4	8	22·0	19·2	3	10	8	9·7	9·0
2	2	6	0·0	5·7	2	7	12	12·4	13·4	2	14	6	0·0	3·4	3	4	9	14·3	12·1	3	10	9	10·2	10·4
2	2	7	19·5	20·9	2	7	13	25·6	24·8	2	14	7	0·0	4·0	3	4	10	14·7	15·5	3	10	10	16·3	15·8

TABLE 1. (*Continued.*)

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	10	11	10 4	10·6	4	2	6	26·1	23·8	4	8	3	10·4	10·0	5	2	0	0·0	7·1	5	9	5	18·1	18·4
3	10	12	15 2	14·9	4	2	7	15·6	13·4	4	8	4	19·9	17·2	5	2	1	23·6	24·1	5	9	6	8·8	7·7
3	11	0	0·0	3·6	4	2	8	13·8	13·4	4	8	5	9·7	9·1	5	2	2	31·7	31·6	5	9	7	10·9	12·3
3	11	1	14·7	11·8	4	2	9	11·5	11·5	4	8	6	24·7	25·8	5	2	3	0·0	6·0	5	10	0	12·2	13·1
3	11	2	22·4	22·3	4	2	10	24·3	23·9	4	8	7	8·8	9·3	5	2	4	24·7	26·8	5	10	1	10·2	10·6
3	11	3	11·3	12·0	4	2	11	0·0	3·7	4	8	8	12·2	9·4	5	2	5	10·2	11·3	5	10	2	10·9	12·2
3	11	4	20·2	21·1	4	2	12	22·7	24·9	4	8	9	0·0	3·0	5	2	6	0·0	5·8	5	10	3	14·3	15·5
3	11	5	19·5	19·3	4	2	13	0·0	3·3	4	8	10	0·0	6·0	5	2	7	18·8	17·8	5	10	4	0·0	4·0
3	11	6	15·4	15·5	4	2	14	9·9	10·8	4	8	11	16·8	16·7	5	2	8	19·0	19·3	5	10	5	8·8	8·3
3	11	7	17·2	17·8	4	3	0	0·0	2·8	4	9	0	0·0	3·3	5	2	9	0·0	4·1	5	10	6	0·0	5·0
3	11	8	22·0	22·1	4	3	1	13·6	13·4	4	9	1	11·5	11·8	5	2	10	19·5	20·7	5	11	0	0·0	0·6
3	11	9	7·4	8·0	4	3	2	42·2	43·0	4	9	2	18·4	20·5	5	2	11	8·1	10·8	5	11	1	10·6	11·3
3	11	10	13·8	14·1	4	3	3	22·9	23·4	4	9	3	24·9	25·6	5	3	0	29·0	30·0	5	11	2	9·9	9·5
3	11	11	8·8	9·5	4	3	4	24·7	23·4	4	9	4	14·3	16·0	5	3	1	17·0	16·5	5	11	3	0·0	3·6
3	12	0	23·8	26·3	4	3	5	11·3	8·9	4	9	5	14·7	15·7	5	3	2	16·1	16·0	5	11	4	10·2	11·2
3	12	1	12·4	13·5	4	3	6	11·8	9·5	4	9	6	0·0	3·3	5	3	3	26·3	26·0	6	0	0	14·7	15·7
3	12	2	0·0	8·5	4	3	7	16·1	14·9	4	9	7	0·0	8·0	5	3	4	16·5	15·3	6	0	1	13·8	13·7
3	12	3	11·5	11·1	4	3	8	38·6	38·4	4	9	8	11·8	12·7	5	3	5	9·7	7·5	6	0	2	0·0	1·3
3	12	4	11·8	13·4	4	3	9	0·0	5·4	4	9	9	22·4	22·1	5	3	6	26·1	26·4	6	0	3	18·6	20·5
3	12	5	14·3	13·9	4	3	10	18·1	20·2	4	9	10	0·0	2·8	5	3	7	0·0	6·2	6	0	4	10·6	7·3
3	12	6	22·4	22·6	4	3	11	9·7	9·7	4	9	11	0·0	5·3	5	3	8	9·5	9·6	6	0	5	13·1	14·1
3	12	8	7·2	8·0	4	3	12	0·0	2·5	4	10	0	15·6	15·1	5	3	9	10·4	11·3	6	0	6	0·0	4·8
3	12	9	12·2	13·2	4	3	13	0·0	2·8	4	10	1	25·4	27·0	5	3	10	8·1	7·7	6	0	7	10·2	9·5
3	12	10	7·2	7·4	4	3	14	15·4	17·0	4	10	2	11·5	13·6	5	3	11	11·8	13·1	6	0	8	0·0	2·2
3	13	0	0·0	0·3	4	4	0	30·8	30·9	4	10	3	0·0	6·6	5	4	0	0·0	1·8	6	1	0	0·0	2·5
3	13	1	14·3	15·8	4	4	1	9·0	9·1	4	10	4	0·0	1·1	5	4	1	10·9	9·6	6	1	1	13·6	15·2
3	13	2	14·5	15·1	4	4	2	18·6	18·8	4	10	5	17·9	14·5	5	4	2	22·0	19·7	6	1	2	0·0	8·2
3	13	3	0·0	6·0	4	4	3	0·0	5·0	4	10	6	8·6	8·9	5	4	3	15·4	17·4	6	1	3	0·0	4·7
3	13	4	14·9	16·9	4	4	4	28·6	27·2	4	10	7	12·7	12·6	5	4	4	25·8	26·1	6	1	4	0·0	4·6
3	13	5	0·0	3·7	4	4	5	35·2	34·3	4	10	8	10·9	10·5	5	4	5	16·5	17·9	6	1	5	19·5	23·1
3	13	6	8·8	9·0	4	4	6	41·5	39·5	4	10	9	6·8	6·6	5	4	6	13·1	16·5	6	1	6	0·0	2·5
3	13	7	9·0	9·9	4	4	7	16·3	15·6	4	10	10	6·1	6·4	5	4	7	15·4	15·7	6	1	7	15·2	18·0
3	13	8	12·0	13·2	4	4	8	33·6	32·1	4	11	0	9·5	8·4	5	4	8	12·9	13·2	6	1	8	0·0	7·5
3	14	0	12·7	11·3	4	4	9	9·9	9·4	4	11	1	13·8	15·2	5	4	9	8·6	9·4	6	2	0	0·0	1·9
3	14	1	9·9	10·4	4	4	10	12·7	12·9	4	11	2	9·7	8·4	5	4	10	10·6	11·7	6	2	1	14·0	17·3
3	14	2	0·0	3·1	4	4	11	0·0	5·8	4	11	3	20·8	21·7	5	4	11	6·1	7·7	6	2	2	0·0	2·6
3	14	3	9·7	10·6	4	4	12	18·1	18·5	4	11	4	10·4	11·5	5	5	0	24·7	24·8	6	2	3	12·9	14·8
3	14	4	12·9	13·4	4	4	13	0·0	5·9	4	11	5	0·0	8·1	5	5	1	12·0	10·9	6	2	4	8·8	10·5
3	14	5	0·0	5·5	4	5	0	0·0	1·9	4	11	6	8·1	7·3	5	5	2	15·9	16·0	6	2	5	12·2	14·3
3	14	6	12·9	13·7	4	5	1	13·6	12·6	4	11	7	9·7	10·6	5	5	3	16·1	18·2	6	2	6	0·0	4·1
3	14	7	0·0	3·0	4	5	2	24·3	24·5	4	11	8	0·0	2·4	5	5	4	10·9	10·8	6	2	7	10·4	11·1
3	14	0	0·0	0·0	4	5	3	23·1	23·0	4	12	0	10·9	9·4	5	5	5	14·0	12·5	6	2	8	0·0	1·8
3	15	1	13·8	15·4	4	5	4	33·1	33·4	4	12	1	17·7	19·1	5	5	6	17·9	18·0	6	3	0	0·0	1·0
3	15	2	10·9	11·0	4	5	5	20·4	16·3	4	12	2	9·0	10·9	5	5	7	0·0	8·6	6	3	1	16·8	20·9
3	15	3	6·1	6·5	4	5	6	0·0	8·4	4	12	3	0·0	4·5	5	5	8	0·0	4·0	6	3	2	9·5	13·7
3	15	4	6·3	6·5	4	5	7	11·3	12·2	4	12	4	0·0	4·4	5	5	9	8·6	9·7	6	3	3	0·0	3·6
4	0	0	67·6	65·9	4	5	8	32·4	30·0	4	12	5	16·3	17·0	5	5	10	11·3	12·1	6	3	4	0·0	3·0
4	0	1	0·0	4·5	4	5	9	19·3	18·7	4	12	6	7·9	2·4	5	6	0	0·0	5·2	6	3	5	15·2	18·4
4	0	2	58·3	55·4	4	5	10	25·8	25·2	4	12	7	14·7	16·2	5	6	1	0·0	5·8	6	3	6	0·0	6·2
4	0	3	14·7	10·6	4	5	11	0·0	6·5	4	13	0	0·0	3·2	5	6	2	13·4	16·7	6	3	7	12·9	15·5
4	0	4	21·1	19·0	4	5	12	0·0	2·5	4	13	1	8·4	8·8	5	6	3	14·9	18·3	6	4	0	0·0	0·2
4	0	5	15·6	14·0	4	5	13	0·0	3·3	4	13	2	0·0	3·9	5	6	4	19·0	20·2	6	4	1	16·5	19·9
4	0	6	39·5	36·7	4	6	0	20·8	19·8	4	13	3	21·1	22·2	5	6	5	14·9	16·2	6	4	2	0·0	8·0
4	0	7	12·7	10·5	4	6	1	24·0	22·5	4	13	4	0·0	5·0	5	6	6	10·2	11·0	6	4	3	14·7	19·9
4	0	8	13·4	12·3	4	6	2	0·0	3·4	4	13	5	5·6	6·0	5	6	7	21·8	21·5	6	4	4	10·4	9·5
4	0	9	0·0	0·3	4	6	3	10·9	8·2	4	14	0	5·4	2·6	5	6	8	8·6	10·0	6	4	5	11·1	11·9
4	0	10	31·7	33·4	4	6	4	30·2	29·2	4	14	1	8·8	7·8	5	6	9	7·4	10·0	6	4	6	0·0	2·4
4	0	11	0·0	3·6	4	6	5	18·1	16·3	5	0	1	32·9	34·1	5	6	10	6·3	8·0	6	4	7	8·4	11·6
4	0	12	24·5	28·0	4	6	6	30·2	29·0	5	0	2	21·5	17·1	5	7	0	19·0	20·1	6	5	0	10·4	12·3
4	0	13	0·0	1·9	4	6	7	18·8	20·6	5	0	3	11·8	10·4	5	7	1	12·9	15·2	6	5	1	19·9	23·2
4	0	14	11·3	12·4	4	6	8	21·5	21·8	5	0	4	13·4	12·8	5	7	2	0·0	10·3	6	5	2	9·3	11·6
4	1	0	0·0	1·5	4	6	9	0·0	4·1	5	0	5	13·4	0·9	5	7	3	12·9	13·5	6	5	3	0·0	5·6
4	1	1	9·5	7·2	4	6	10	0·0	1·1	5	0	6	0·0	3·0	5	7	4	10·6	10·2	6	5	4	0·0	5·7
4	1	2	55·4	54·2	4	6	11	11·1	11·8	5	0	7	10·4	8·8	5	7	5	18·6	19·7	6	5	5	11·8	13·4
4	1	3	21·1	21·5	4	6	12	7·9	9·4	5	0	8	24·5	25·2	5	7	6	12·4	13·0	6	5	6	9·5	10·3
4	1	4	42·2	40·6	4	6	13	14·0	16·0	5	0	9	8·6	9·4	5	7	7	15·6	15·1	6	6	0	0·0	6·2
4	1	5	0·0	5·3	4	7	0	12·7	12·9	5	0	10	18·1	20·4	5	7	8	0·0	7·5	6	6	1	7·7	8·3
4	1	6	0·0	2·3	4	7	1	0·0	7·1	5	0	11	7·0	7·4	5	7	9	10·9	10·8	6	6	2	11·8	14·2
4	1	7	11·8	8·7	4	7	2	22·0	23·0	5	0	12	7·7	6·7	5	8	0	10·6	10·8	6	6	3	13·4	15·5
4	1	8	33·6	32·4	4	7	3	23·1	22·5	5	1	0	41·5	42·5	5	8	1	11·5	10·6	6	6	4	8·6	9·3
4	1	9	0·0	5·4	4	7	4	24·3	22·1	5	1	1	13·4	11·8	5	8	2	14·3	13·8	6	6	5	6·1	7·2
4	1	10	19·3	19·8	4	7	5	17·2	16·9	5	1	2	0·0	7·9	5	8	3	17·9	19·5	6	7	0	9·3	12·2
4	1	11	14·9	13·4	4	7	6	9·3	2·6	5	1	3	21·5	19·9	5	8	4	10·4	8·2	6	7	1	11·8	14·0
4	1	12	0·0	1·2	4	7	7	0·0	4·4	5	1	4	0·0	6·1	5	8	5	9·7	10·3	6	7	2	0·0	4·7
4	1	13	0·0	2·4	4	7	8	15·9	17·0	5	1	5	12·4	10·4	5	8	6	0·0	7·4	6	7	3	5·9	5·2
4	1	14	19·3	21·3	4	7	9	17·9	16·5	5	1	6	29·5	30·4	5	8	7	15·2	15·8	6	7	4	9·3	11·7
4	2	0	47·2	47·3	4	7	10	16·3	15·2	5	1	7	0·0	3·7	5	8	8	8·8	8·5	6	8	0	0·0	2·0
4	2	1	9·3	7·3	4	7	11	0·0	8·4	5	1	8	13·1	13·3	5	9	0	0·0	0·0	6	8	1	5·4	5·2
4	2	2	33·6	34·9	4	7	12	0·0	6·8	5	1	9	21·5	22·3	5	9	1	12·4	12·7	6	8	2	9·9	11·2
4	2	3	0·0	2·8	4	8	0	18·1	15·2	5	1	10	12·7	12·5	5	9	2	11·1	10·2					
4	2	4	26·3	25·9	4	8	1	33·1	33·6	5	1	11	0·0	7·7	5	9	3	8·1	9·6					
4	2	5	36·1	35·4	4	8	2	19·9	11·1	5	1	12	8·6	10·4	5	9	4	9·5	10·1					

A perspective drawing of the molecule, and superimposed sections of the three-dimensional electron-density distribution taken through the atomic centers, are shown in Fig. 1. The bond distances and valency angles, with their standard deviations calculated from the least-squares residuals, are shown in Fig. 2. All the intermolecular contacts less than 4·0 Å were calculated and are listed in Table 3.

TABLE 2.

Atom	Final positional parameters (fractional) x	y	z	Final anisotropic thermal parameters ($\times 10^4$) b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
As(1)	0·1305	0·4818	0·1659	241	46	32	−4	−33	−20
Cl(2)	−0·1196	0·5858	0·2465	491	49	44	−35	94	−59
N(3)	−0·2282	0·4773	−0·0164	307	54	25	−10	−46	−40
C(4)	−0·1678	0·3165	0·1912	335	42	42	−13	−7	7
C(5)	−0·3629	0·2545	0·1754	341	47	51	−5	19	22
C(6)	−0·5215	0·2698	0·1003	344	41	45	−12	−23	−12
C(7)	−0·4750	0·3461	0·0372	245	54	42	−24	−67	−2
C(8)	−0·2700	0·4079	0·0499	178	36	40	−31	0	25
C(9)	−0·1248	0·3935	0·1312	149	39	34	−11	−66	−1
C(10)	0·3277	0·6197	0·0395	200	46	53	+3	−37	−10
C(11)	0·3495	0·6747	−0·0411	335	46	56	−9	59	−20
C(12)	0·1799	0·6622	−0·1132	286	65	43	−0	61	−7
C(13)	−0·0110	0·5969	−0·1030	328	57	31	−1	2	22
C(14)	−0·0374	0·5409	−0·0213	177	33	52	−10	27	−28
C(15)	0·1366	0·5526	0·0516	261	46	35	−2	−65	−20

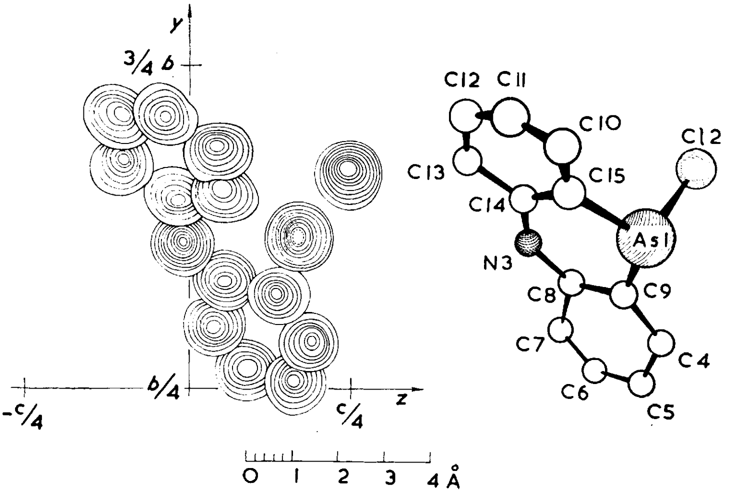

FIG. 1. Superimposed sections of the three-dimensional electron-density distribution, taken through the atomic centres parallel to (100). Contours start at 1 e Å^{-3} and are at intervals of 1 e Å^{-3} except for the As(1) and Cl(2) which start at zero and are at intervals of 5 e and 2·5 e Å^{-3}, respectively. A perspective drawing of the molecule is also shown.

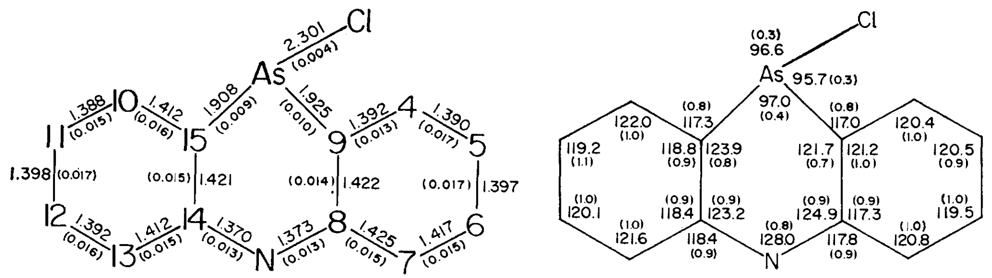

FIG. 2. Bond lengths (Å) and valency angles (degrees) in phenarsazine chloride. Standard deviations are given in parentheses.

TABLE 3.

Shorter intermolecular distances (Å).

All crystallographically-independent contacts ⩽4·0 Å between a standard molecule (1) and neighbouring molecules are listed.

Atom (molecule 1)	to Atom	in Molecule	*d*	Atom (molecule 1)	to Atom	in Molecule	*d*
As(1)	C(12)	8	3·88	C(4)	C(12)	8	3·88
				C(4)	C(12)	15	3·97
Cl(2)	N(3)	15	3·60	C(4)	C(13)	15	3·63
Cl(2)	C(4)	4	3·68	C(5)	C(7)	3	3·96
Cl(2)	C(5)	4	3·70	C(5)	C(12)	15	3·67
Cl(2)	C(13)	15	3·90	C(5)	C(13)	15	3·85
				C(6)	C(7)	3	3·92
N(3)	C(6)	3	3·81	C(6)	C(7)	7	3·55
				C(6)	C(8)	7	3·55
				C(7)	C(7)	3	3·97

Molecule			
1	x	y	z
3	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
4	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
7	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
8	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
15	$-\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$

The mean plane through the twelve carbon atoms was calculated and the displacements from the plane suggested some deviation from planarity. Accordingly the mean plane through each of the phenyl rings was calculated. The plane through carbon atoms numbered **4** to **9** (Fig. 1) has equation:

$$0{\cdot}58171\,X - 0{\cdot}59819\,Y - 0{\cdot}55115\,Z = -4{\cdot}67686$$

and the plane through carbon atoms numbered 10 to 15 has equation

$$0{\cdot}57104\,X - 0{\cdot}71348\,Y - 0{\cdot}40600\,Z = -5{\cdot}35895$$

where X, Y, and Z are co-ordinates in Å referred to the crystal axes. The angle between the normals to these two planes is 10° 40′. The deviations of the atoms from each of the planes are given in Table 4.

TABLE 4.

Deviations of the atoms from the mean planes through the phenyl rings.

	Deviation (Å) from plane through carbon atoms numbered			Deviation (Å) from plane through carbon atoms numbered	
Atom	4 to 9	10 to 15	Atom	4 to 9	10 to 15
As(1)	−0·224	0·022	C(9)	−0·029	0·302
Cl(2)	−2·521	−2·260	C(10)	0·252	0·003
N(3)	0·108	0·004	C(11)	0·499	−0·007
C(4)	0·002	0·584	C(12)	0·631	0·006
C(5)	0·022	0·681	C(13)	0·487	−0·001
C(6)	−0·018	0·470	C(14)	0·224	−0·002
C(7)	−0·007	0·224	C(15)	0·107	0·002
C(8)	0·030	0·178			

DISCUSSION

Three crystalline forms of phenarsazine chloride, a stable green form and two metastable yellow phases, have been reported previously.[11] The present investigation suggests the existence of only one form of (unsolvated) phenarsazine chloride, which is bright yellow when powdered and yellowish green as single crystals, although the green colour may be due to traces of impurity formed in the severe heating necessary for crystallization. The metastable crystals from a variety of solvents contain solvent of crystallization (in the case

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[11] Fischer, *Mikrochemie*, 1933, **12**, 257.

of xylene half a molecule per molecule of phenarsazine chloride), which is rapidly lost when the crystals are removed from the mother-liquor.

The details analysis of the structure of the solvent-free crystals has established that the phenarsazine chloride molecule is slightly folded about the As · · · N axis, the angle between the two *o*-phenylene groups being 169° 20′, and the chlorine atom being outside this angle. Each ring is thus displaced by only about 5° from a completely planar arrangement, and these deviations are probably not large enough to permit isolation of stable geometrical isomers. The deviations of the atoms (Table 4) from the *o*-phenylene planes indicate that the arsenic and nitrogen atoms are situated accurately on the plane through C(10)–C(15), but are significantly displaced, in opposite directions, from the C(4)–C(9) plane. These displacements indicate a slight twisting of the group C(4)–C(9), in addition to the folding of the molecule about the As · · · N axis. This twisting is probably a result of crystal-packing forces; Table 3 shows that, of the sixteen shortest intermolecular contacts, thirteen involve atoms of the twisted ring.

The As–Cl bond (2·30 ± 0·004 Å) is significantly longer than the distances reported [12] for arsenic trichloride (2·16 Å) and dimethylarsenic chloride (2·18 Å), but is about the same length as the corresponding bond in chlorodiphenylarsine (2·26 ± 0·02 Å).[13] It is difficult to account for these differences, although the steric effects of the large phenyl groups might be involved. The As–C bonds (mean length 1·917 ± 0·007 Å) are significantly shorter than the normal single-bond distance (for example, 1·990 ± 0·019 Å in cacodyl disulphide[14]). The C–N distances (mean 1·371 ± 0·009 Å) are also significantly less than the single-bond length (1·48 Å),[12] and are about the same length as the C–N bond in aromatic amines (1·371 Å in *p*-nitroaniline [15] for example). The As–C and C–N lengths suggest an extended aromatic system in phenarsazine chloride, involving interaction of the arsenic and nitrogen lone pair electrons with the *o*-phenylene π-electrons, with in addition possibly d_π–p_π bonding between the π-electrons and vacant 4*d* orbitals of the arsenic atom. The mean aromatic C–C distance is 1·406 ± 0·005 Å, and although there are some variations none of the individual lengths differs significantly from the mean value.

The Cl–As–C angle (mean value 96·1 ± 0·2°) is normal for tervalent arsenic, and is similar to the corresponding angle in chlorodiphenylarsine (96 ± 1°).[13] The C–As–C angle (97·0 ± 0·4°) is significantly smaller than the values of 105—106° in other arsenic–phenyl compounds,[13,16] probably as a result of strain due to the cyclic nature of the molecule and to its near-planarity. The C–N–C angle (128 ± 0·9°) is significantly larger than normal, again indicating some strain in the central ring.

The intermolecular distances (Table 3) all correspond to van der Waals interactions, and do not require special comment.

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[12] Sutton *et al.*, " Table of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.

[13] Trotter, *Canad. J. Chem.*, 1962, **40**, 1590.

[14] Camerman and Trotter, *J.*, **1963**, 219.

[15] Trueblood, Goldish, and Donohue, *Acta Cryst.*, 1961, **14**, 1009.

[16] Trotter, *J.*, 1962, 2567.