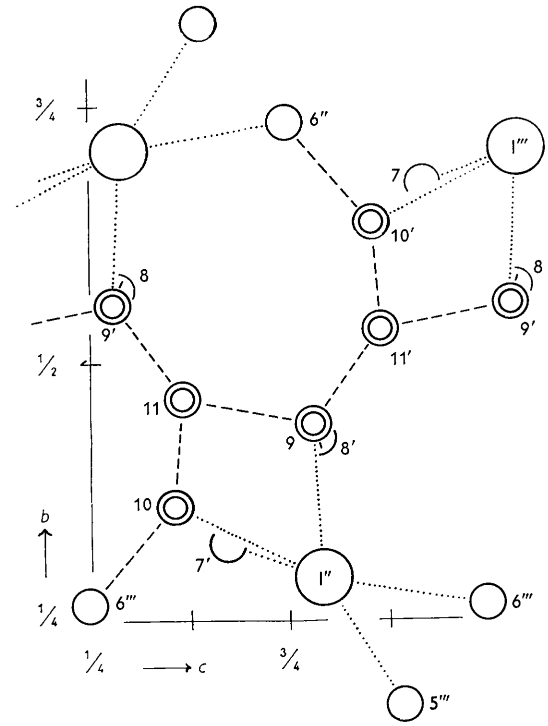

Fig. 1. Zigzag chain of water molecules and iodine atoms in (+)-demethanolaconinone hydroiodide trihydrate (Przybylska, 1961), viewed along the *a* direction (+*a* into paper), origin of figure at 1/4 *b*, 1/4 *c*. Labelling of atoms as in Tables 1 and 2. Large circles, iodine atoms; small single circles, hydroxyls; small double circles, water molecules. Dashed lines show hydrogen bonds among oxygens; dotted lines show hydrogen bonds to iodine.

situated at a distance of 5 Å *from the nitrogen atom of the alkaloid, it seems unlikely that the hydrogen of* HI *is attached to nitrogen. It follows that one of the oxygen atoms associated with iodine may be an acceptor of the hydroiodide proton. Since* ∠C9–O6···O10 *is* 112°, *it is possible that hydroxyl* (O6) *is donating a proton to* O10 *and accepting the proton of* HI. Following this reasoning, water (O9) presumably accepts a proton from hydroxyl (O8′)(∠C12–O8′–O9 = 116°), and donates one to the iodine. Water (O10) donates one proton to the iodine. There remain four water protons, one on O9, one on O10, and two on O11, to be assigned among the remaining three hydrogen bonds around the water molecules. Further refinement of the structure might clarify the proton assignment in this interesting hydrogen-bond scheme.

Similar zigzag chains involving water molecules and halogen atoms have been found in other halogeno alkaloid hydrates, *e.g.* codeine hydrobromide dihydrate (Lindsey and Barnes, 1955; Kartha, Ahmed and Barnes, 1962), and strychnine hydrogen bromide dihydrate (Robertson and Beevers, 1951). Such chains may prove to be a frequent feature in structures containing large organic molecules among which halogen atoms and several crystallographically distinct water molecules must be fitted.

Table 2. *Bond angles around water molecules and iodine atom*

Water molecules		Iodine atom	
Atoms†	Angle‡	Atoms†	Angle‡
I″–O9–O11	100°	O5‴–I″–O6‴	52°
I″–O9–O11′	141	O7′–I″–O9	59
I″–O9–O8′	105	O7′–I″–O10	66
I″–O10–O6‴	100	O9–I″–O10	67
I″–O10–O11	101	O9–I″–O6‴	103
O8′–O9–O11	101	O7′–I″–O6‴	128
O8′–O9–O11′	87	O10–I″–O5‴	133
O11–O9–O11′	114	O7′–I″–O5‴	140
O11–O10–O6‴	124	O9–I″–O5‴	153
O9–O10–O9′	134	O10–I″–O6‴	157
O9–O11–O10	89		
O9′–O11–O10	134		

† Atoms located as described in the footnote of Table 1; see also Fig. 1.

‡ All data taken from Przybylska (1961) for calculations of bond angles using SILLIAC program V-19 by Dr F. M. Lovell, University of Sydney. Errors estimated by present author: I–O–O ± 6°; O–O–O ± 10°.

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An analysis of possible methods for refining a non-centrosymmetric structure containing a partial centre of symmetry.

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Srinivasan (1961) has shown that, in non-centrosymmetric structures containing a partial centre of symmetry, 'inverse overlap' can occur between one atom and another related to it by inversion through this centre. He has demonstrated that the diagonal approximation to the least-squares matrix will not be valid when inverse overlap occurs, since the terms corresponding to interactions between the overlapping atoms are of significant magnitude.

Inverse overlap occurs much more frequently than is often realized. It exists, for example, when a molecule containing one heavy atom crystallizes in one of the non-centrosymmetric space groups which have a centrosymmetric projection and an arbitrary positional parameter perpendicular to this projection (*e.g.* $P2$, $P2_1$, $C2$). Having encountered the problem in several structure analyses (*e.g.* Duffield, Jefferies, Maslen & Rae, 1963), we have examined various refinement techniques to see which is the most suitable for this type of problem. All have been found to be unsatisfactory.

1. *Full-matrix least-squares*

Inverse overlap is an example of the effect, discussed by Geller (1961), of strong interaction between the terms of the least-squares matrix.

The term corresponding to the interaction between the x coordinates of the ith and jth atoms is a_{ij}, where

$$a_{ij} = \sum_{hkl} \frac{\partial|F_c|}{\partial x_i} \frac{\partial|F_c|}{\partial x_j} . \quad (1)$$

This can be expressed (Srinivasan 1961) in the form

$$a_{ij} = \sum_{hkl} \frac{2\pi^2}{a^2} h^2 f_i f_j [\cos(\theta_i - \theta_j) - \cos(\theta_i + \theta_j - 2\alpha)] . \quad (2)$$

The diagonal term, a_{ii}, is given by

$$a_{ii} = \sum_{hkl} \frac{2\pi^2}{a^2} h^2 f_i^2 [1 - \cos 2(\theta_i - \alpha)] . \quad (3)$$

The conditions for inverse overlap between the ith and jth atoms are

$$\theta_i + \theta_j \simeq 0, \quad 2\alpha \simeq 0 . \quad (4)$$

Applying these to equations (2) and (3), and assuming the ith and jth atoms to be of the same type($f_i = f_j$), then

$$a_{ij} \simeq -\sum_{hkl} \frac{2\pi^2}{a^2} h^2 f_i^2 (1 - \cos 2\theta_i) \simeq -a_{ii} \quad (5)$$

and, where the mth is any other atom,

$$a_{jm} \simeq -\sum_{hkl} \frac{2\pi^2}{a^2} h^2 f_i f_m [\cos(\theta_i - \theta_m) - \cos(\theta_i + \theta_m)] \simeq -a_{im} . \quad (6)$$

Thus there is an approximate linear dependence between the ith and jth rows of the least-squares matrix, which is therefore ill-conditioned. The shifts calculated for the ith and jth atoms will be unreliable, and the standard deviations on these positions will be large. Reliable parameters can be obtained for the atoms not subject to inverse overlap, although it may first be necessary to combine the ith and jth rows of the least-squares matrix.

2. *Diagonal least-squares*

If inverse overlap is the only significant interaction, $a_{ik} \simeq a_{jk} \simeq 0$, and the full least-squares equations for the ith and jth shifts tend to

$$a_{ii}(\Delta x_i - \Delta x_j) = D_i \quad (7)$$

where

$$D_i = \sum_{hkl} (|F_o| - |F_c|) \frac{\partial|F_c|}{\partial x_i} . \quad (8)$$

The apparent shift yielded by the diagonal least-squares approximation is $\Delta x_i'$, where

$$\Delta x_i' = D_i / a_{ii} . \quad (9)$$

Comparison of (7) and (9) leads immediately to the result

$$\Delta x_i' = \Delta x_i - \Delta x_j \quad (10)$$

That is, the shift deduced from the diagonal approximation is equal to the difference between the real atomic shift and the real shift corresponding to the atom at the inverse position. The shifts calculated for the atoms not affected by inverse overlap will be correct, assuming that all other interaction terms are small.

3. *Fourier methods*

The shift formulae corresponding to the Fourier and difference Fourier refinement techniques are essentially the same as those given by the least-squares method (Lipson and Cochran, 1953). It is clear, therefore, that equation (10) will hold for these methods also. The observed slope in the difference synthesis, for example, at the position of an atom subject to inverse overlap will be equal to the difference between the slopes corresponding to the real shift in the atom and the real shift in its inverse.

It is clear that, for structures affected by inverse overlap, accurate refinement of the parameters of the overlapping atoms is not possible using any of these methods, although reliable parameters may be obtained for those atoms which do not overlap inversely. The full-matrix least-squares approach has the advantage that the presence of inverse overlap can be deduced immediately from the size of the standard deviations, or by examining the correlation matrix (Geller, 1961). This may, however, be outweighed, at least in the earlier rounds of refinement, by the computational difficulties involved in the full-matrix solution, particularly as the other methods refine reliably those atomic positions not affected by inverse overlap.

As indicated by Srinivasan (1961), the inverse overlap is mathematically very similar to direct overlap in projection analysis. In fact, results identical with the above, apart from some changes in sign, hold for direct overlap.

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