Short Communications

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The use of Edsac II for the direct determination of crystal structures.

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A method for the determination of possible sets of signs for the Fourier coefficients of a two-dimensional electron-density map, using the electronic computer Edsac I, has been described by Cochran and Douglas (1955, 1957), whose notation we shall use in this short note without redefining the terms used. Recently we have been able to use the computer Edsac II, which is some sixty times faster than its predecessor. The opportunity has been taken to reconstruct all programs so that more of the initial work is done by the machine, and improvements have been made which result in fewer sets of signs (of which of course only one set can be correct) being retained by the machine following the first stages of the calculation.

The work now proceeds in the following stages:

(*a*) The machine is supplied with a table of values of unitary structure factors (values of $|U(\mathbf{h})|$). It then finds all sign relationships of the form

$$Y(\mathbf{h}, \mathbf{h}') \equiv S(\mathbf{h})S(\mathbf{h}')S(\mathbf{h}+\mathbf{h}') \approx +1\,,$$

which involve unitary structure factors whose magnitudes are greater than some specified limit. The sign $S(\mathbf{h})$ of each such $U(\mathbf{h})$ is then expressed as far as possible in terms of the quantities $Y(\mathbf{h}, \mathbf{h}')$.

(*b*) The machine rejects all sets of signs for the structure factors which fail to pass two tests:

(i) More than some specified proportion of all the $Y(\mathbf{h}, \mathbf{h}')$ must be positive.
(ii) For each relevant value of **h** the quantity $\sum_{\mathbf{h}'} Y(\mathbf{h}, \mathbf{h}')$ must not be less than some specified limit, which can usually be taken as zero.

After this stage two possibilities are open.

(*c* i) For each set of signs which have passed the earlier tests the machine evaluates:

$$T = \sum_{\mathbf{h}} \left||U(\mathbf{h})| - \alpha|G(\mathbf{h})|\right| \div \sum_{\mathbf{h}} |U(\mathbf{h})|\,,$$

where

$$G(\mathbf{h}) = \sum_{\mathbf{h}'} U(\mathbf{h}')U(\mathbf{h}+\mathbf{h}')$$

and α is a scaling factor which varies slowly with $|\mathbf{h}|$ and is found by the machine in the course of the calculation. For a structure composed (in projection) of approximately equal atoms the correct set of signs is characterised by a lower value of T than that for any incorrect set—see the first two entries in the Table below. Even when the atoms are unequal (in the examples given in the Table, because of overlap in projection) the correct set of signs may be expected to give a value of T near the lower end of the range.

(*c* ii) Alternatively the machine evaluates electron-density maps for each set of signs. Numbers are printed out on a grid with spacings which can be varied to correspond roughly to various unit-cell dimensions, and the maps are then contoured by hand. (An Edsac program for presenting contoured electron-density maps on a cathode ray screen will be described by M. Wells in a forthcoming publication). The machine took about forty seconds per Fourier synthesis in a representative example; of this only a few seconds represent computing time, most of the time is used in putting out the result in the form of punched tape, which is subsequently run through a teleprinter. When faster output on magnetic tape, or direct cathode ray contouring, becomes possible, it is questionable whether it will be worth while to apply tests subsequent to stage (*b*), (such as that mentioned under (*c* i), or the more versatile test described by Woolfson (1958)) rather than to proceed straight away to the evaluation of electron-density maps. Some illustrative results are given in Table 1.

Table 1. *Some illustrative results*

Compound studied	Number of sets of signs at end of stage (*b*)	Value of T for correct sets of signs	Values of T [for other sets
Nitroguanidine	27	0·27	0·53 to 0·76
Dimethyl-arsanthren dibromide	3	0·31	0·51
Alloxantin	8	0·45	0·45 to 0·64
Xylose	16	0·56	0·55 to 0·82

The correct solutions for nitroguanidine and for xylose were known in advance. Our solution for dimethylarsanthren dibromide was found to be the same as Dr Sutor had obtained by inspection of its Patterson function. It will be seen that in the case of xylose (already commented on by Woolfson (1958) in this connection) and possibly also in the case of alloxantin, it would not have been possible to narrow the search to only one set of signs at the end of stage (*c* i). For alloxantin the correct solution was in fact chosen by inspection of eight electron-density maps; values of T were worked out later as a matter of interest. This projection of the structure has since been refined by conventional methods.

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References

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