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A comparison of anisotropic differential Fourier and least-squares refinement.

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The announcement of a complete matrix anisotropic least-squares refinement program for the IBM 704 by Busing & Levy (1959), at a recent computer conference, provided us with an opportunity to compare the results of this program with those from an anisotropic differential Fourier synthesis refinement program which had been written for the IBM 650 by Shiono (1959).

The data used were those for the crystal structure of $S_3C_4H_4$, 4-methyl-1,2-dithia-4-*cyclo*pentene-3-thione, a 64 parameter problem (including a scale factor) in space group $P2_12_12_1$ which had been completely refined, first by isotropic then by anisotropic Fourier methods (Kehl & Jeffrey, 1958; Jeffrey & Shiono, 1959).

This crystal structure analysis was one in which not only the high absorption coefficient but also the nature of the crystals led to appreciable and perhaps systematic errors in the experimental observations. It was therefore also of interest to compare the estimates of the accuracy of the analysis as deduced by Cruickshank's (1949) method making use of the atomic curvatures and by the least-squares procedure.

The final parameters (coordinates and anisotropic temperature factors) from the anisotropic differential synthesis were applied to the least-squares program for the minimization of $\omega(F^2_{\text{obs.}}-F^2_{\text{calc.}})^2$. The Hughes (1941) weighting system was used. Unobserved reflections were included with $F^2_{\text{obs.}}=0$ and $\omega=(1/16F^2_{\text{min.}})^2$. After three cycles on the 704, each of which took 40 min., the parameter changes were negligible. The results are summarized in Table 1. The complete data are available on request from the authors. The standard deviations, (s.d.)s, computed from the two methods agree very closely. This is in contrast to the result reported by Ibers & Cromer (1958) in which they found a factor of two when they applied both methods to the analysis of $Ce(IO_3)_4H_2O$.

For the coordinates, the differences between the results of the two methods, $\Delta x_i = x_{i(DS)} - x_{i(LS)}$, in terms of the standard deviations were distributed as follows: 16 parameters with Δx_i less than 2(s.d.), 4 between 2(s.d.) and 3(s.d.), and one greater than 3(s.d.) and less than 4(s.d.). The corresponding figures for the thermal parameters were 38, 3, 1. There were no apparent systematic trends in the differences.

It is concluded that for this structure analysis, there is no significant difference between the results of the two refinement procedures. This is in agreement with the general theory of Cochran (1948) and Cruickshank (1952).

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Table 1. *Comparison of differential synthesis,* (*DS*), *and least squares,* (*LS*), *refinement for* $S_3C_4H_4$

	Average and maximum differences in atomic coordinates in Å				Average and maximum differences in thermal parameters in Å^2			
	$\overline{\Delta x_i}$	Δx_i (max.)	s.d.$_{(DS)}$	s.d.$_{(LS)}$	$\overline{\Delta B_{ij}}$	ΔB_{ij}(max.)	s.d.$_{(DS)}$	s.d.$_{(LS)}$
S_1	0·0087	0·010	0·005	0·005	0·149	0·41	0·29	0·21
S_2	0·0071	0·017	0·005	0·005	0·144	0·22	0·27	0·19
S_3	0·0076	0·015	0·006	0·006	0·428	1·04	0·31	0·23
C_3	0·0335	0·053	0·017	0·019	0·612	2·30	1·01	0·74
C_4	0·0206	0·045	0·017	0·019	0·676	1·15	0·98	0·76
C_5	0·0126	0·024	0·019	0·020	0·801	1·62	1·01	0·84
C_6	0·0239	0·038	0·030	0·026	0·878	2·91	2·00	1·34

The bond lengths for the two refinements

	DS	*LS*	s.d.
S_1–S_2	2·05 Å	2·04 Å	0·007 Å
S_1–C_5	1·71	1·68	0·020
S_2–C_3	1·75	1·76	0·019
S_3–C_3	1·63	1·65	0·019
C_3–C_4	1·43	1·38	0·025
C_4–C_5	1·38	1·37	0·027
C_4–C_6	1·48	1·51	0·034

The atom designations are as given in the previous paper (Jeffrey & Shiono, 1959).