Short Communications

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Acta Cryst. (1956). **9**, 615

On the unreliability of the 'reliability index'.

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(*Received* 25 *April* 1956)

Although it has frequently been pointed out that the so-called 'reliability index', $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$, is not a trustworthy measure of the correctness of a structure or of the relative accuracy of different structures, it is still used in these ways to a considerable extent. There have been several recent examples of incorrect structures for which reasonably low overall R values were reported. These include β-selenium (Burbank, 1952; Marsh, Pauling & McCullough, 1953), 2,2′-di-(1,3-dioxacyclopentyl) (Furberg & Hassel, 1950), *p*-nitroaniline (Abrahams & Robertson, 1948; Donohue & Trueblood, 1956), diacetylene dicarboxylic acid dihydrate (Dunitz & Robertson, 1947), purpurogallin (Dunitz, 1952), and triphenylene (Klug, 1950; Vand & Pepinsky, 1954; Pinnock, Taylor & Lipson, 1956). None of the above contains disproportionately heavy atoms, which tend usually to accentuate the difficulty of deciding, on the basis of R alone, whether or not a structure is correct (Lipson & Cochran, 1953).

Some of these structures have been discussed recently in scattered places, usually in the course of a review or a particular structure determination. It is the purpose of this note to draw attention specifically to this problem and to urge all who are active in structure determination by X-ray methods to study these examples carefully. The last two will not be discussed here; no details concerning purpurogallin have yet been published, and the incorrect and presumably correct triphenylene structures have been reviewed in detail recently by Pinnock *et al.* (1956).

In each of the other four structures the situation is similar in that the R values for certain classes of reflections (with which one could distinguish the correct and incorrect structures) were significantly greater than for other (non-distinguishing) classes, the reported incorrect Fourier projections showed distorted peaks and some spurious maxima, and, at least for the first three compounds as well as for triphenylene, the incorrect structures were all featured by an abnormal distance or other unusual structural feature. Each of these difficulties was eliminated in the correct structure. Burbank (1952) was able to refine his incorrect projection of the ($hk0$) data for β-selenium only to 30·8%, although the other two zones gave an R of 18·7%; in the correct projection, R for ($hk0$) fell to 17·5%. Furberg & Hassel (1950) could not refine their incorrect projection to give R below 38%; the corresponding correct projection gave an R of 13%. Dunitz & Robertson (1947) were unable to refine their incorrect ($0kl$) projection to give R less than 30%; for the correct projection, the final R was 14·8%. As an experiment, we attempted to refine the incorrect *p*-nitroaniline structure of Abrahams & Robertson (1948) by eight cycles of least squares; R for the ($h0l$) reflections fell to 13·0%, while that for ($hk0$) was 25·8%, and that for ($0kl$) was 30·3%. The ($h0l$) projection was correct, the other two were incorrect. The overall agreement index was 20·1%. Since these values were obtained with individual anisotropic temperature factors for each atom, and slightly different scale factors and individual parameters for each zone, they are not strictly comparable to the corresponding values (18·2, 22·1, and 18·5%) for the correct structure, for which an overall isotropic temperature factor and single scale factor (which increase R by about 4%) were used (Donohue & Trueblood, 1956). They do, however, demonstrate that a quite respectable overall agreement index may be obtained with an incorrect structure.

Clearly one must not only always examine carefully the individual observed and calculated amplitudes, paying particular attention to any serious and possibly systematic discrepancies, but also examine critically the electron-density distributions, and be especially wary of very peculiar structural features. It is undoubtedly significant that structural abnormalities are present in most of the incorrect structures cited here and in other similar discussions (Lipson & Cochran, 1953); these features are what usually led to the further investigation of what had been, or might have been, assumed correct. Obviously many spurious structures may not have structural anomalies serious enough to have provoked critical re-examination.

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