If a reflection has a small value of P_{ii}, but its F value is discrepant, it becomes an "outlier." This may result from an inadequate model as well as from systematic error. Least squares will try to fit this reflection, with a resulting introduction of bias. In these circumstances a robust/resistant variant of least squares [Nicholson, Prince, Buchanan & Tucker, Crystallographic Statistics, Ramaseshan, Richardson & Wilson, eds. Indian Acad. Sci. Bangalore, pp 229-263 (1982)] is useful because it helps to identify the outliers and reduces the sensitivity of the model to them. In their multiple refinements of the structure of D(+)-tartaric acid, using data from the Single-Crystal Intensity Measurement Project of the IUCr, Hamilton & Abrahams [Acta Cryst. A26, 18-24 (1970)] used $\sigma_i = 0.1|F_o|$ to determine the weights. The assumption was that there was a sufficiently small number of very weak reflections that any effect of overweighting would be minor. Analysis of the projection matrix, however, shows that there is a small number of very weak reflections with $P_{ii} > 0.95$, whereas more than 20% of all reflections, mostly relatively strong, have $P_{ii} < 0.1$. Furthermore, a small number of weak reflections provides the dominant influences on all parameters except scale and extinction. In a few cases a parameter is determined overwhelmingly by a single reflection, and in many cases the parameter is determined by a small subset of the data. Nearly half of the reflections do not appear among the five most influential ones for any parameter! The structure is therefore determined by a subset of the data, far smaller than the full set, consisting mainly of weak reflections. The rather large scatter among different data sets of parameter estimates, relative to the computed standard deviations, that was found by Hamilton & Abrahams is therefore probably ascribable to the imbalance of weights between weak and strong reflections.

17.7–3 MODEL-STRUCTURES ILLUSTRATING THE PRESENCE OF FALSE LEAST-SQUARES R1-MINIMA AND THEIR RESOLUTION WITH R2-REFINEMENT, A.L.Spek, Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, University of Utrecht,3508 TB Utrecht, The Netherlands.

The crystallographic literature contains a few well documented cases where the refinement converged to a minimum that was later shown to be false but very close to the true one. In such cases the derived geometry shows features that may be chemically intriguing and statistically significant but that actually are refinement artefacts. A good example is the low-temperature structure of adamantane (Nordman&Schmitkons, Acta Cryst. (1965),18,764) for which it was shown (Donohue&Goodman, Acta Cryst.(1967),22,352) that the reported unusual variation in related bond-distances and angles was due to refinement to a false R1-minimum. The true R1-minimum was reached by rigid group refinement on a regularized molecule followed by the release of the constraints

We recently used this example to test the hypothesis that this false minimum is in fact an artefact of the R1-refinement. The SHELX-76 package was modified for this purpose to include R2-refinement facilities. It was indeed found that the true minimum could be reached easily with an R2-refinement starting from the false

Minimizing R1 as opposed to R2 is a commonly used procedure for structure refinement and seems to be mainly dictated by the wide availability of program packages that consolidate a practice from the past that was mainly introduced for computational reasons that no longer apply. R2-refinement is usually advocated as a facility to include 'negative' observed intensities in the refinement. However, the above example shows that there can be other benefits as well, since, although R1 and R2 (when properly weighted) give essentially the same parameter values for the true minimum, their behavior outside this minimum is quite different.

A two parameter model was constructed that exhibits the same refinement behavior as the adamantane structure but in a parameter space that is more accessible for exhaustive investigation, the results of which will be presented.