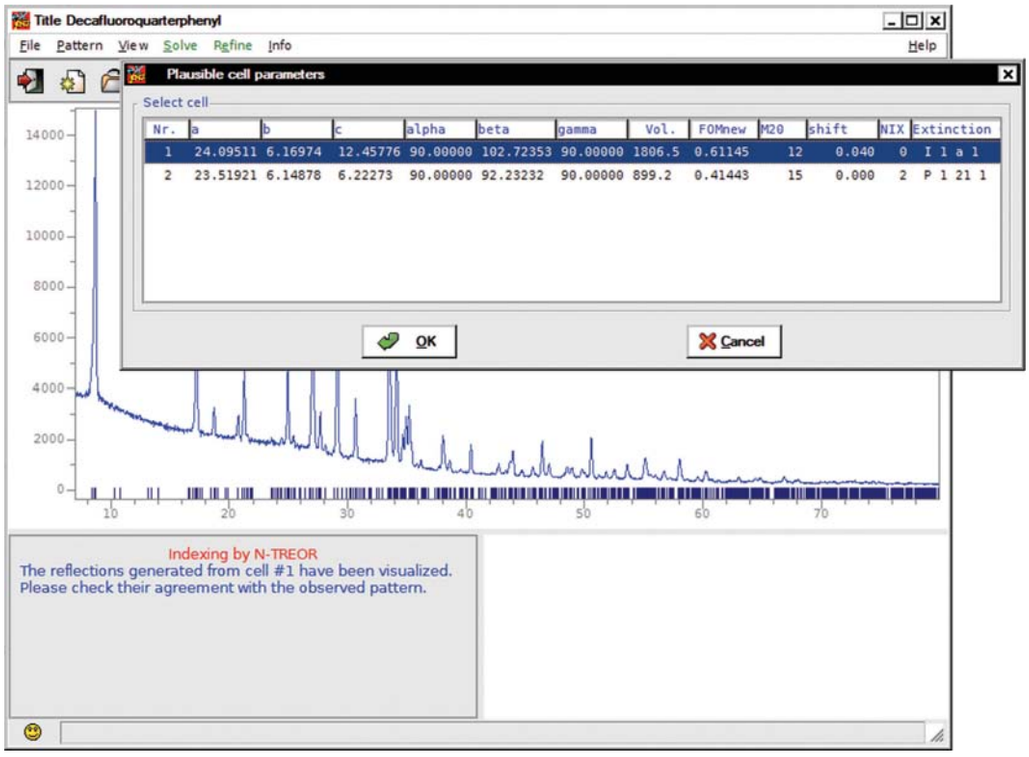

Figure 3.4.1
The list of possible cells for the decafluoroquarterphenyl structure automatically found using *N-TREOR09*.

The 2θ values of the first 25 peaks, in the range 5–25°, were determined by *WinPLOTR* and supplied to *DICVOL06*. The first 20 peaks were used for searching for the solution. No plausible cell was found when assuming that no impurity was present and exploring all the systems (from cubic to triclinic). *DICVOL06* was also unsuccessful when the non-default strategies of extended search and data correction for zero-point error were considered (by setting some flags to 1 in the input file). If it was supposed that two impurity lines might be present among the peaks (by setting the flag corresponding to the maximum number of accepted impurity/spurious lines to 2), *DICVOL06* was able to find the following monoclinic cell: a = 8.7480 (36), b = 8.6313 (32), c = 7.6077 (26) Å, β = 97.201 (33)°, with two unindexed lines, M_{18} = 41.5, F_{18} = 125(0.0041, 35). The refinement of the cell by considering all the 25 lines gave a = 7.6087 (26), b = 8.6295 (30), c = 8.7459 (34) Å, β = 97.201 (34)°, which is very similar to the published one; 23 indexed lines, M_{20} = 30.1, F_{20} = 102.6(0.0048, 41). The presence of the two impurity lines has been ascribed by the authors to a small amount of hexagonal plastic phase.

Example 2

Cu(II)–Schiff base complex (Banerjee *et al.*, 2002). Published information: $Cu(C_{15}H_{12}NO_2)_2$, triclinic, a = 11.928 (4), b = 12.210 (5), c = 9.330 (5) Å, α = 102.54 (4), β = 111.16 (5), γ = 86.16 (4)°, $P\bar{1}$, experimental range 6–100° 2θ, λ = 1.54056 Å, RES = 1.22 Å, high-quality X-ray laboratory data, indexed by *DICVOL91*. The 2θ values of the first 30 peaks, in the range 6–25°, were determined by *WinPLOTR* and supplied to *DICVOL06*. The first 20 peaks were used for searching for the solution. If it was assumed that no impurity was present, no plausible cell was found down to the monoclinic system. When the triclinic system was explored, *DICVOL06* suggested only one plausible solution: a = 12.2157 (73), b = 12.2031 (77), c = 9.3071 (41) Å, α = 65.798 (46), β = 102.572 (59), γ = 95.711 (61)°, with no unindexed lines, M_{20} = 27.0, F_{20} = 77.0(0.010, 26). The refinement of the cell considering all the 30 lines gave a = 12.2125 (65), b = 12.1989 (61), c = 9.3016 (32) Å, α = 65.826 (33), β = 102.569 (40), γ = 97.755 (44)°, no unindexed lines, M_{20} = 27.9, F_{20} = 72.8(0.0106, 26). For this, the corresponding conventional cell is a = 11.93313 (61), b = 12.2125 (65), c = 9.3016 (32) Å, α = 102.569 (40), β = 111.152 (33), γ = 86.151 (44)°, similar to the published one.

3.4.4.6.2. *Indexing using N-TREOR09*

Two examples of powder diffraction pattern indexing by using *N-TREOR09,* as implemented in the *EXPO* program, will be described. To activate the procedure some specific instructions must be given to *EXPO via* the input file or the graphical interface. As a first step, the peak-search procedure is automatically performed on the experimental powder pattern and the list of corresponding d values are supplied to *N-TREOR09*. During the indexing process a correction for zero-point error is automatically carried out (positive and negative shifts are taken into account). Both the examples below were successfully indexed by a default run of *EXPO*.

Example 3

Decafluoroquarterphenyl (Smrčok *et al.*, 2001). Published information: $C_{24}H_8F_{10}$, monoclinic, a = 24.0519 (9), b = 6.1529 (3), c = 12.4207 (5) Å, β = 102.755 (2)°, $I2/a$, experimental range 7–80° 2θ, λ = 1.79 Å, RES = 1.39 Å, medium-quality X-ray laboratory data. The first 43 peaks (in the range 7–67°) with intensities greater than a default threshold were selected (an intensity-based criterion is automatically adopted). The first 25 lines were used to find a possible cell that was then refined by considering all the 43 peaks. At the end of the automatic indexing procedure, *N-TREOR09* suggested two possible cells ranked according to WRIP20 [equation (3.4.5)], as shown in Fig. 3.4.1 (WRIP20 is denoted as

FOMnew in *N-TREOR09*). The first one in the list is the correct cell. It is worth mentioning that the classical M_{20} figure of merit was not able to pick up the solution. The best cell parameters, found according to FOMnew, were a = 24.0951 (50), b = 6.1697 (21), c = 12.4578 (37) Å, β = 102.724 (18)°, similar to those reported in the literature, with FOMnew = 0.61, M_{20} = 12; all the lines in the pattern were indexed. The program provided the solution thanks to its automatic check for a zero-point correction (2θ zero shift = 0.04°) and was able to correctly identify the extinction group (*I_a_*). For the second suggested cell (the wrong solution) FOMnew = 0.41, M_{20} = 15, and two lines were unindexed.

Example 4

Hexagonal turkey egg-white lysozyme (Margiolaki *et al.*, 2005). Published information: hexagonal, a = 71.0862 (3), c = 85.0276 (5) Å, $P6_122$, experimental range 0.4–12° 2θ, RES = 3.35 Å, synchrotron data. The first 94 peaks (in the range 0.4–6°, λ = 0.700667 Å) with intensities greater than a default threshold were selected. An intensity-based criterion was automatically adopted. The first 25 lines were used to find possible cells that were then refined by considering all 94 peaks. Five possible unit cells were automatically suggested by the program in the following systems: hexagonal (1), orthorhombic (1) and monoclinic (3). The highest value for WRIP20 was 0.99, and was for the correct hexagonal cell parameters: a = 71.0922 (4), c = 85.0269 (7) Å, which are similar to those reported in the literature; all the 94 selected lines in the pattern were indexed. For this cell, the program detected a geometrical ambiguity (see Section 3.4.2.2) between hexagonal and orthorhombic lattices and automatically selected the higher-symmetry one.

3.4.5. Conclusion

Indexing a powder diffraction pattern is sometimes described as a 'gateway technology', because the determination of the cell parameters is so fundamental: if no cell has been identified the execution of the subsequent steps of the structure solution process is impossible, and if a wrong cell has been used the correct solution is unreachable. Therefore extremely close attention must be paid to the indexing step of the process. From the early 1970s, the increasing interest in powder pattern indexing and the progress seen, in terms of both methods and algorithms, have strongly contributed to opening the door to modern applications of powder diffraction techniques. The availability of a quite large number of software packages, based on different indexing strategies, enables the scientist interested in solving crystal structures to switch from one program to another when the first fails, so increasing the possibility of success. In some cases indexing is still a challenging process. Good-quality data are necessary and careful inspection of each indexing step, in particular in the selection of the experimental peak positions to be used, is advisable.

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