Chiral tetrahedral AB$_4$ molecules or molecular fragments, where A and B are atoms, are common, yet handedness assignment rules for these species, to the best of our knowledge, do not exist. We propose a simple set of rules for such an assignment and apply it to many chiral molecules; to a chiral crystal—quartz—identifying preservation of handedness across its phase transition; and to a large random population of chiral AB$_4$ structures. The concept of handedness-labelling is discussed by presenting a second alternative for labelling.

1. Introduction

While the common image of tetrahedral AB$_4$ species is that they are achiral (because of molecules such as CH$_4$, CCl$_4$, etc.) the largely unnoticed reality is that the majority of tetracoordinated molecules or molecular fragments are chiral. The main origins of this chirality are the facts that it is quite rare to find perfect tetrahedricity of AB$_4$ (in crystals, in the adsorbed state, in amorphous materials, in clusters and so on), and that this distortion from ideality, much more often than not, is such that the resulting structure has no mirror plane (or an $S_n$ symmetry element). Collected in the first two columns of Table 1 are some examples of common tetrahedral structures, which although not recognized as such, are chiral. One can identify chirality either qualitatively by inspection of the structure and its coordinates, or quantitatively, by measuring the degree of chirality (third column; zero on this scale is achirality). Examples of genuine AB$_4$ achiral structures of course exist, and are collected at the bottom of the table for the sake of providing the full picture.

Since the chirality of solids is a prime parameter in heterogeneous catalysis, in chromatographic separations and in optics—to mention just few key applications—the question of the associated handedness, emerges. To the best of our knowledge, there are no official, IUPAC-accepted rules for assigning left- or right-handedness to AB$_4$ elementary building blocks, where A and B are atoms. It is perhaps of relevance to mention here that handedness rules have been proposed for some related cases, none of which are applicable, however, for the simple AB$_4$ case. These include the rules for chiral octahedral six-coordinated complexes, tris-bidentate octahedral complexes, A(B–B)$_3$, that can be applied in principle to bidentate A(B–B)$_2$ systems, the Cahn–Ingold–Prelog (CIP) rules for conformational chirality of A(C–X)$_4$, helical rules which require the existence and identification of a $C_2$ symmetry axis, and perhaps also the rules for spiro compounds, where one considers the central atom.

Herein we report a simple set of rules for handedness assignment of tetrahedral chiral AB$_4$ structures. We recall that labelling an object as ‘left’ or ‘right’ is arbitrary; in chemistry and physics it has simply been a matter of agreed convention. Therefore, when one approaches the handedness-labelling of a family of objects, which is not covered by existing labelling methods, due to the arbitrariness of the problem, all options are open. However, we have decided to develop a labelling method, which is as close as possible in its rational to the labelling rules, which are currently used for four-coordinated structures, namely,