Phosphoramides and thiophosphoramides: some different structural aspects investigated based on the structures deposited in the Cambridge Structural Database (CSD) completed with new diffraction studies

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The structural features of phosphoramides and thiophosphoramides are reviewed and compared with the structures of the phosphorous (V) compounds with the [N][*X*][*Y*]P═O and [N][*X*][*Y*]P═S segments (N = nitrogen atom & *X*, *Y* = N, C, O), considering the diffraction experiments of some derivatives and analysis of the structures deposited in the Cambridge Structural Database (CSD). The main topics investigated are related to "the geometries of molecules" and "the aggregations of molecules in the crystals", with focus on the hybridization properties of some atoms, the strengths of bonds, the values of bond angles and the hydrogen bonds geometries, and also trying towards finding some "empirical rules" for prediction of crystal structures from molecular structures. Among these structures, the bond-angle sums are analyzed at the nitrogen atoms (P—N—*Y* + *Y*—N—*X* + *X*—N—P) for the structures with a nitrogen atom in a three-coordinated [*X*][*Y*][N]P environment (*X* and *Y* are any atoms from CSD), to evaluate the trend of nitrogen atoms towards sp^2 or sp^3 hybridization in different families of phosphorous-nitrogen compounds. For the nitrogen atoms in the non-planar geometry, the orientations of lone electron pairs (LEPs) located at the nitrogen atoms with respect to the P═O and P═S bonds are discussed. For the structures with the *X*—O—P segment and a few structures with the *X*—S—P segment, the corresponding bond angles are considered at the oxygen and sulfur atoms. The histograms of P═O bond lengths are studied in different families of phosphoryl compounds as well as a similar study for the P═S containing compounds. The P—N, P—O, P—S and P—C bond lengths are also considered. These studies help us to achieve some insight about the electronic properties in different segments of the molecules. The electronic properties are also studied for the other atoms/segments with potential application as "H-bond donor" or "H-bond acceptor" site. Moreover, for some of these segments, the orientations, or at least the most preferable orientations, are studied with the CSD analysis as they are important on the aggregations of molecules in the crystal structures. Furthermore, the strength capabilities of "H-donor" and "H-acceptor" sites are studied in the crystal structures of phosphoramide and thiophosphoramide derivatives in which the competition between different acceptor sites and also between different donor sites are also considered through a statistical analysis based on the CSD. Then, the geometries of hydrogen bonds are discussed based on the characteristic N—H…O hydrogen bonds in the structures with an [NH]P(O) segment with considering the motifs based on such hydrogen bonds and the histograms of N…O distances and N—H…O angles. Similar investigation is studied for the structures with an [NH]P(S) segment. The "donor-directionality" and the "acceptor directionality" concepts are also discussed.

Keywords: Crystal Structure; Cambridge Structural Database (CSD); Phosphoramide; Thiophosphoramide