Within a project on systematic analysis of anion environments we have undertaken a Cambridge Structural Database search of the free picrate anion: 99 structures having R<0.10, σ<0.010 Å and located H atoms were retrieved. The H-bonding capability of picrate is mainly due to the negatively charged phenolic oxygen: out-of 80 structures of picrates containing one or more potential HB donor groups, 79 form at least one D-H...O bond (DHO>90°, H...O<3.0 Å), one shows strong S...O-interactions, while in the 19 structures with no HB donors the phenolic oxygen interacts only with C-H groups pointing to it. Although each of the three nitro groups may act as HB acceptor, it is worth mentioning the role played by ortho-NO2: most of the D-H...O interactions are bifurcated, with the H atom bonded both to the phenolic and to the nearest ortho-NO2 oxygen. Intermolecular associations of picrate may involve one, two, but no more than three D-H...O bonds (D=O,N; all NH are positively charged or belong to a positively charged moiety). When only one HB donor is present, the crystal inevitably consists of ion pairs, held together by rather strong HBs (distances down to 2.52 and 2.62 Å for O...N and O...O, respectively). All OH groups lie close to the picrate phenyl plane, whereas NH groups can approach the anion from all possible directions, OH being more accessible than aminic or amidic NH. With two HB donors we can get pairs again, as well as less common molecular associations, such as H-bonded infinite chains or 4-membered rings. Chains and rings are the more interesting cases: each picrate forms two HBs, one above the phenyl plane, one under. As for the HB distances, we have so far studied their dependence on the number of HBs formed, on the chemical nature of the donors (O or N), and on charge: their dependence on HB donors pKas, as well as the comparison with related compounds (dichloroacetic, picric acid, phenols) are under investigation.

According to our opinion, the great variety of HB patterns and especially the frequent formation of an ion pair between the positively charged moiety and the picrate anion, strongly tightened by short HBs, can explain the successful use of picrate salts in crystallization processes.