Poster

Unraveling the mysteries of intramolecular hydrogen bonding defined by the phosphoryl group

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The term hydrogen bonding has an over 100-year history, and research on this phenomenon is of enduring interest. Hydrogen bonds (HBs) are the driving force for organocatalytic reactions, the formation of transition metal complexes, drug···protein interactions, and the assembly of biological structures as proteins and the DNA duplex. Since studies revealed a mixed nature of hydrogen bonding where not only electrostatics govern the stability and topology of HBs, determination of other components (*i.e.*, charge transfer interactions, charge transfer assistance, cooperativity effect, Pauli repulsions, dispersion, and secondary electrostatic interactions) assess the utility of the particular system as a molecular or supramolecular synthon [1-3].

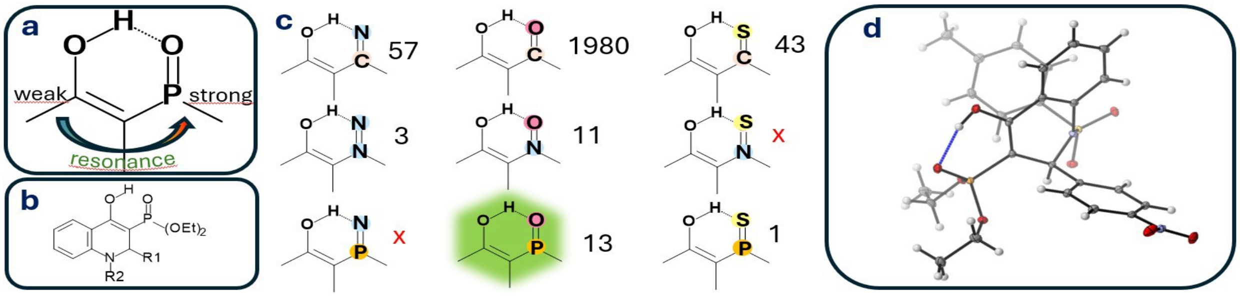

Figure 1. (a) The intramolecular hydrogen bond between enol and phosphoryl groups supported by a resonance effect within a conjugated system; (b) The structural scheme of derivatives forming O-H···O=P intramolecular bonding; (c) The number of structures deposited in Cambridge Structural Database containing particular motif. The intramolecular HB formed by enol and phosphoryl groups is highlighted in green; (d) Crystal structure of the compound stabilized by hydrogen bond defined by O-H···O=P synthon.

Our studies focus on phosphorylated hydroquinolinoles prone to form intramolecular hydrogen bonds between the enol and phosphoryl groups (*Fig.1a*) [4]. Cambridge Structural Database (CSD) has been reported 13 structures containing such motifs so far. The formation of a planar *quasi*-ring by the hydrogen bond suggests resonance-assisted hydrogen bond (RAHB) observation [4]. However, the geometrical parameters of the HB shed new light on the nature of the observed interaction. To date, reports on RAHB focus on homo- or heteronuclear hydrogen bonds linked through a conjugated carbon chain. This trend is well reflected by the number of structures deposited in CSD containing particular chains linking donors and acceptors (*Fig. 1b*). Therefore, the geometrical regime for RAHBs is assumed only for such systems. Reports on the influence of heteroatoms on the nature of this type of interaction are very scarce. The structures were characterized using a single crystal X-ray diffraction experiment (SCXRD) (*Fig.1d*) and supported by spectroscopic characterization of their solutions (^{1}H NMR, ^{31}P NMR and ^{13}C NMR). These data confirmed the existence of O-H···O=P synthon within the series. Additionally, the intramolecular interactions stabilizing the *quasi*-ring have been characterized using QTAIM and NBO methods.

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