C═O···π Interaction: A Rare Noncovalent Binding in Phosphoramide Structures

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In the structure of $C_6F_5C(O)NHP(O)[N(C_2H_5)(C_6H_{11})]_2$, in addition to N—H···O═P hydrogen bond, the oxygen atom of P═O group is involved in the P═O···π interaction (O_P···Cg = 3.507 Å, Cg is the centroid of C_6F_5 ring). Moreover, a noncovalent C═O···π interaction takes part in the crystal packing, O_C···Cg = 3.159 Å. The C═O···π interaction is the novel feature of this structure, as a CSD analysis [1] (version 5.34, May 2013 update) of 136 structures with a $C(O)NHP(O)[N]_2$ skeleton shows that such interactions exist only in 2 structures [2].The dihedral angle between the aromatic ring and the plane defined by the atoms of [C][N]C═O segment is 66.66°. The C═O bond length in the present structure (1.215(18) Å) is within the expected values of analogous structures deposited in the CSD (1.18 to 1.33 Å). The P═O (1.483(10) Å) and P—N (1.634(12) Å and 1.642(12) Å) bond lengths are standard for phosphoric triamides [3]. The bond angle sums around the nitrogen atoms (SUM = 2 × P—N—C + C—N—C) are 357.8° and 352.0° that show few deviations from the planar value of 360°. The more pyramidal N atom is oriented so that the corresponding lone electron pair is *anti* with respect to the P═O group.

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References:

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