

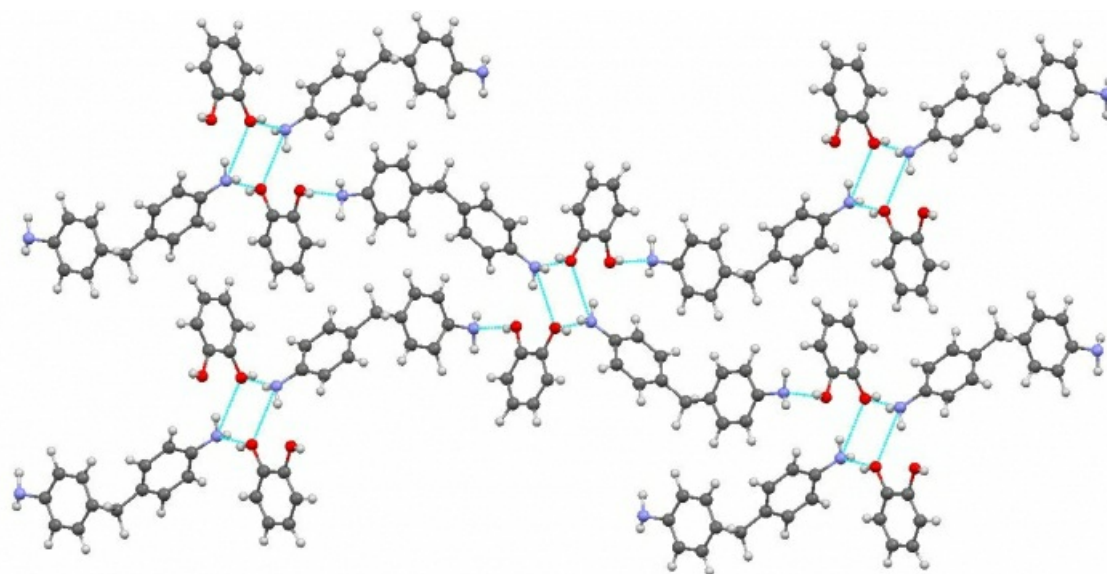
*Rationalisation and prediction: A curious case of aniline-phenol recognition*Ankush Sood¹, Gautam R. Desiraju¹¹SSCU, Indian Institute of Science, Bangalore, India

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Aniline-phenol recognition is remarkable for the structural diversity it displays owing primarily to the hydrogen bonding groups that are tetrahedral and contain unequal but stoichiometrically complementary donor and acceptor atoms. Further, there is higher conformational freedom than in the well-known acid-amide recognition. It is argued that these unique properties account for trends specific to supraminols, like the absence of polymorphism, ease of cocrystal formation, large number of synthons, and sensitivity of the crystal packing and synthon employed towards the chemical, geometrical and steric attributes of the molecule. The latter makes this recognition ideal to study the effects of isostructurality and interaction interference on packing. A well-known example is that of the interference between hydrogen bonding and herringbone interactions studied by Allen et al., wherein, a correspondence between molecular and crystal structure is not observed and ortho-, meta- and para-aminophenol, all show packing similar to benzene. In such a case, amino and hydroxy groups compromise on their hydrogen bonding potentials and weak hydrogen bonds are formed. In a recent study, we engineered seven cocrystals of dianilines and diphenols and studied their packing in the backdrop of 90 plus crystal structures of supraminols, single and multicomponent, in CCDC. The components of cocrystals were chosen so as to vary chemical, geometrical and steric factors independently or simultaneously to enquire whether the known synthons in supraminols are conserved or further structural divergence occurs. The results of this study, assisted with an extensive literature review, indicate that the synthons in this family are now well established and their prediction based on the molecular parameters is possible. While the crystal packing in these cocrystals and other supraminols can be rationalised, its prediction remains challenging, despite the prediction of synthon, in part due to the very nature of aniline-phenol recognition.

[1] Allen, F.H. et al. (1997). *J. Am. Chem. Soc.* 119 (15), 3477-3480.

[2] Sood, A., Desiraju, G.R. (2017). *Struct. Chem.* 28, 173-199.



Windmill arrangement in 4,4'-methylenedianiline.catechol cocrystal

Keywords: [crystal engineering](#), [cocrystal](#), [hydrogen bonding](#)