Electron Density Distributions in 2-(dimethylamino)biphenyl-2'-carboxaldehydes

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The amine and the aldehyde groups of 2-(dimethylamino)biphenyl-2'-carboxaldehydes (Fig. 1) are non-coplanar, and the N lone pair electrons are in a favorable position for potential overlap with the carbonyl C atom's π^* wavefunction. This interaction between the electrophilic C and the amine N atoms has been discussed elsewhere [1]. The discovery that the N-to-carbonyl distance was actually shorter in the methyl-substituted analog prompted a high-resolution investigation of the distributions of electron density in these molecules [1]. 49124 Mo K_α reflections (mean $I/\sigma(I)$ = 30.8, measured to θ = 47.25°) of a crystal of the unsubstituted biphenyl were collected at 110 K. 41381 Mo K_α reflections (mean $I/\sigma(I)$ = 23.0, measured to θ = 41.29°) of a crystal of the methyl-substituted biphenyl were collected at 100 K. Atomic positions and anisotropic thermal parameters were achieved via Hirshfeld Atom Refinement [2]. Both experimental and theoretical structure factors were used in the multipole refinements to test which model is most believable [3]. Deformation density maps and electrostatic potentials suggest that the interaction between the molecules' amine and aldehyde groups is largely electrostatic. AIM analyses reveal that: in the unsubstituted biphenyl, the N has a charge of -1.02, the carbonyl C has a charge of +1.03, and the N-to-C interaction has a bond order of 0.024; and, in the methyl-substituted biphenyl, the N has a charge of -1.00, the carbonyl C has a charge of +0.98, and the N-to-C interaction has a bond order of 0.057 [4].

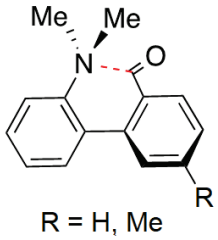

Fig 1. 2-(dimethylamino)-biphenyl-2'-carboxaldehyde, with interaction between amine and aldehyde groups indicated.

References

[1] Work submitted to *CG&D* in March 2019.
[2] Capelli, S. *et al.* (2014). *IUCrJ* **1**, 361-379.
[3] Tonto program for refining crystal structures using *ab initio* wavefunctions and fitting electronic wavefunctions to X-ray diffraction data (http://sourceforge.net/projects/tonto-chem).
[4] AIMAll (Version 17.11.14), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2017 (aim.tkgristmill.com).