

s9.m3.p7 **Molecular Packing Analysis of Molecular Complexes of N,N-Dimethylaniline.** T. Dahl, *Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway*

Keywords: molecular interactions, charge transfer interactions.

Crystal structures are known of 4 molecular complexes of N,N-Dimethylaniline.¹⁻⁴ In all these complexes N,N-Dimethylaniline and the partner acceptor molecule are stacked alternately, as in most other electron-donor-acceptor complexes. Regarding intermolecular distances in the stack and degree of non-planarity of the amino group there are, however, large differences between the complexes.

A molecular packing analysis of the complexes has been performed, based on atom-to-atom potentials, using the computer program PCK83.⁵ The main purpose was to study the effects of intermolecular interactions, as e.g. charge transfer interactions, which may be present in addition to ordinary van der Waals interactions. It was assumed that differences between the molecular packing in the experimental structure and the packing giving the lowest calculated lattice energy are mainly results of such additional interactions.

By this procedure a relatively coherent picture has been obtained. There seems to be a strong correlation between the strength of the additional interaction on the side of the N,N-dimethylaniline molecule where the lone pair electrons of the amino group are located, the degree of non-planarity of the amino group, and the electron affinity of the acceptor molecule. There seems to be some additional interaction also on the opposite side of the N,N-dimethylaniline molecule, but the strength of this interaction seems to be approximately the same for all the complexes.

s9.m3.p8 **Modification of Roothaan equations for the ab-initio calculation of Interactions in Large Molecular Systems in the absence of Basis Set Superposition Error.** M. Sironi, A. Famulari, F. Moroni, M. Raimondi, *Dipartimento di Chimica Fisica ed Elettrochimica and Centro-CNR (CSRSRC), Università degli Studi di Milano - via Golgi, 19 - 20133 Milano, Italy.*

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The Roothaan equations have been modified to compute molecular interactions between weakly bonded systems at the SCF level of theory to avoid the introduction of the basis set superposition error (BSSE)¹. An efficient algorithm compatible with the usual formulation of the analytic derivatives of the SCF energy has been implemented including geometry gradient optimisation in both the direct and conventional approaches².

The method was incorporated into the GAMESS-US package and tested on different hydrogen bonded systems of biological interest³. The results show the computational advantage of the *a priori* exclusion of the BSSE: sufficiently accurate results are obtained by small basis sets of 3-21G quality.

The strategy is applied to the study of the conformations of DNA base pairs including structure and energetics of the complex between the cytosine-guanine pair and the $[cis-Pt(II)(NH_3)_2]^{++}$ cation⁴. The most stable predicted geometries of the planar and non planar N₇-O₆ chelate $[cis-Pt(NH_3)_2-(N_7-O_6)Guanine-Cytosine]^{++}$ system are reported. The results so far presented provide complementary information to the experimental crystallographic data available.



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