

### Serendipitous Rediscovery of Three Polymorphs of Benzidine

Michal Rafilovich, Joel Bernstein, *Department of Chemistry, Ben-Gurion University of the Negev, Be'er Sheva, Israel, 84105*. E-mail: rafilovi@bgumail.bgu.ac.il

The search for a co-crystal of benzidine (4, 4'-biphenyldiamine) as a donor with potential acceptors has revealed three polymorphs of the source material benzidine for which, somewhat surprisingly, no structure has been reported according to a CSD search Nov. 2003.

For about 130 years, benzidine and its derivatives had very wide industrial use, mainly as dyes and pigments in a variety of applications. By the middle 1970's the use of benzidine totaled 0.5-1 million kg. At that time the compound itself was found to be carcinogenic, and its commercial use has essentially been abandoned, apparently along with interest in its structure and properties.

The biphenyls attracted the attention of many crystallographers [1 and references therein]. One of the principle reasons for interest in this compound was the fact that in the gas phase the molecule had been shown to be non-planar, while in the crystal the molecule's presence on a crystallographic inversion center requires it to be planar.

The three reported structures are characterized by the molecules packing of  $Z' > 1$  (1.5, 3 and 4.5), which according to the CSD are found in only 0.25%, 0.4% and 0.002% of the total structures.

The three forms were grown from two component solutions (one is benzidine) as well as from solutions of benzidine only. In some crystallization experiments the polymorphs grew concomitantly [2].

[1] a) Brock C. P., Minton R. P., *J. Am. Chem. Soc.*, 1989, **111**, 4586-4593; b) Brock C. P., *J. Res. Natl. Inst. Stand. Technol.*, 1996, **101**, 321-325. [2] Bernstein J., Davey R. J., Henck J. -O., *Angew. Chem. Int. Ed.*, 1999, **38**, 3440-61.

**Keywords:** polymorph, co-crystal, concomitant crystallization