

m13.o04**Phase Transitions, Polymorphism and Photochromism of Salicylideneaniline**Frédéric Arod^a, Philip Pattison,^{a,b} Kurt Schenk,^a Gervais Chapuis^a^aLaboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne, Switzerland. ^bSNBL-ESRF, Grenoble, France. E-mail: frederic.rod@epfl.ch**Keywords: photochromism, phase transitions organic, structure-property relationships in solids**

Organic compounds exhibiting photo- or thermochromicity are of considerable interest owing to their properties and possible applications. The photochromism of salicylideneaniline (SA) was discovered by Senier *et al.* at the beginning of last century, and in 1964, Cohen *et al.* [1] observed its polymorphism. It is generally accepted that the stable form of SA in the ground state is the enol form, with an intramolecular hydrogen bond between the hydroxyl proton and the nitrogen atom. Upon photoexcitation of this enol form with UV light, it undergoes an ultrafast proton transfer from the hydroxyl group to the nitrogen, due to the electronic redistribution in the excited state. The proton transfer generates a keto tautomer in the excited state. We report on the alpha-2-polymorph structure of SA in the ground state [2]. We also describe a new polymorph, beta, which features a planar SA molecule and is therefore thermochromic. We did also revisit the alpha-1-polymorph structure of SA described by Destro *et al.* [3], but reconsidering their hypothesis. We suggest a lowering of the symmetry with the aim to improve the structure solution.

- [1] Cohen, M. D.; Schmidt, G. M. J.; Flavian, S. *J. Chem. Soc.* 1964, 2041-2051.
 [2] Arod, F.; Gardon, M.; Pattison, P.; Chapuis, G. *Acta Cryst.* 2005, C61, o317-o320.
 [3] Destro, R.; Gavezzotti, A.; Simonetta, M. *Acta Cryst.* 1978, B34, 2867-2869.

m13.o05**Analysis of strong and weak inter- and intramolecular interactions in the crystals of carborane derivatives.**

Ivan Glukhov, Konstantin Lyssenko, Alexander Korlyukov, Mikhail Antipin

A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, Moscow, Russian Federation. E-mail: ivglukh@gmail.com

Keywords: inter- and intramolecular interactions, electron density distribution in bonds, topological properties of charge distribution

Within the framework of the systematic studies of the electron density distribution function ($\rho(\mathbf{r})$) in the crystals of carboranes the high-resolution X-ray diffraction study was carried out for a number of carborane-containing compounds. As the experimental $\rho(\mathbf{r})$ studies for the carborane derivatives are quite rare, we have analyzed in details the peculiarities of the reconstructed $\rho(\mathbf{r})$ with the usage of R. Bader's theory "Atoms in Molecules" (AIM) and compared them with the ones, obtained by the DFT calculations for the same compounds. On the basis of the obtained results we have tried to make a deeper insight to their geometrical and electronic structures. The following conclusions were made:

1. The electrons of the carborane moiety are distributed all over the polyhedron and it is very often the reason of the problems, connected with the reconstruction of the experimental $\rho(\mathbf{r})$. We have worked out some general recommendations how to refine the data for such systems with strong delocalization of the electrons.
2. The unusual properties of the C-C bond in the *o*-carborane were analyzed. So, in the crystal of 8,9,10,12-tetrafluoro-*o*-carborane the C-C bond corresponds not to the shared-type of interactions, but to the intermediate-type according to the AIM terminology. Then, the presence of the Π -electron back-donation from the phenyl ring to the antibonding orbital of the C-C bond was established for the C-aryl substituted carboranes. Finally, analysis of the available literature data as well the application of the AIM theory to some DFT calculations allowed us to state, that the C-C bond in the carborane can be described as a "single Π -bond" what the reason for its unusual properties is. We have applied these data also to the understanding of the value of the C-C bond length in some metal-lacarboranes derivatives.
3. It became possible for three isomeric molecules: 1-phenyl-*o*-carborane, 3-phenyl-*o*-carborane and 1-phenyl-*m*-carborane to get a qualitative agreement between the theoretical and experimental values of their relative energies by the integration of the $\rho(\mathbf{r})$ within the atomic basins of all these molecules. Also It was shown, that despite the presence of the shortened contacts between the hydrogen atoms of the phenyl ring and the carborane moiety the interaction between these atoms is attractive, what is clear from the presence of the (3,-1) critical point between them, and is the reason of the very low value of the barrier to the rotation of the phenyl ring in these compounds.
4. Also, the application of the AIM theory allowed us to find the network-forming interactions in the crystals of carboranes in which the conventional H-bonds are absent. It was shown that in this case namely the B-H...H-X (X=B,C) interactions play the dominating role in the formation of the crystal structure. Summing up all interactions we have estimated the lattice energy for the studied compounds and compared it with the theoretical ones, obtained in the PW-DFT calculations. They have proved to be in a good agreement.

This work has been supported by Russian Foundation for Basic Research (grant no. 06-03-32557).