

# The Molecular Structures of the Three Disilylbenzenes Determined in the Gas Phase, the Solid State and by *ab initio* Calculations

Norbert W. Mitzel<sup>a</sup>, Paul T. Brain<sup>b</sup>, Michael A. Hofmann<sup>b,c</sup>, David W. H. Rankin<sup>b</sup>, Robert Schröck<sup>a</sup>, and Hubert Schmidbaur<sup>a</sup>

<sup>a</sup> Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany.

<sup>b</sup> Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K.

<sup>c</sup> Present address: BASF AG, Global Research Agricultural Products, 67056 Ludwigshafen, Germany

Reprint requests to Dr. N. W. Mitzel. Fax +49(0)89 289 13147. E-mail: N.Mitzel@lrz.tum.de

Z. Naturforsch. **57 b**, 202–214 (2002); received November 26, 2001

Silylbenzenes, Gas Phase Structure, Electron Diffraction

The molecular structures of four silylbenzenes (benzenes with H<sub>3</sub>Si-substituents), *viz.* silylbenzene, 1,2-, 1,3- and 1,4-disilylbenzene, were studied by electron diffraction in the gas phase and by *ab initio* calculations. The structures of 1,2- and 1,4-disilylbenzene were also determined by X-ray diffraction experiments on single crystals grown *in situ*. The results are compared and discussed with the focus on the evaluation of the SARACEN method for the analysis of gas-phase data, and particularly on its ability to deal with small structural distortions. Important experimental structural parameters are the Si-C bond lengths [Å] and the *ipso* C-C-C angles [deg], which are 1.863(3) / 118.2(2) for gaseous silylbenzene ( $r_{\alpha}$ ), 1.875(2) / 119.9(2) for gaseous and 1.870(2) / 118.7(av) for solid 1,2-disilylbenzene, 1.871(1) / 119.4(3) for gaseous 1,3-disilylbenzene, 1.870(2) / 119.0(2) for gaseous and 1.866(3) / 117.4(2) for solid 1,4-disilylbenzene. The angle distortions in the benzene ring geometries are analysed and interpreted in terms of an additivity rule of the distortion caused by each of the silyl substituents. This additivity scheme predicts excellently the observed structures of the silylbenzenes and is in best agreement with the structures calculated *ab initio*. The slight distortion of molecular symmetry in the crystal structures makes a detailed comparison of the solid-state values impossible, but on average they are in good agreement with theory and predictions of the additivity model. The gas-phase values obtained by the SARACEN method show less pronounced distortions of the benzene ring geometries than observed or predicted by the other methods, but the trends of distortion are fully consistent.