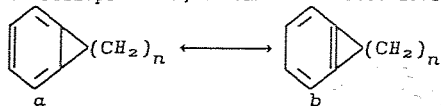


09.1-4 THE QUESTION OF BOND FIXATION IN FUSED BENZENE RINGS. By R. Boese and D. Bläser, Institut für Anorganische Chemie, Universität-GH Essen, Universitätsstr. 5-7, D-4300 Essen 1, W.-Germany

With decreasing n of fused alkylene rings to benzene one of the Kekulé-structures (a,b) were assumed to be preferred (W. E. Billups et al, J. Am. Chem. Soc. 1973, 7878)



PE. spectra and ab initio calculations (E. Heilbrunner et al, Chem. Ber. 106, 961 (1973), Y. Apeloig, D. Arad, J. Am. Chem. Soc. 1986, (3241) as well as structure determinations of substituted benzocyclopropenes and -butenes indicated that no bond fixation (a,b) occurs for n = 1 (1) rather than a distortion by strain resulting in shorter fused bond lengths. For n = 2 (2) and for (1.2,4.5)-benzodicyclobutene (3) a smaller influence on the fused bond lengths is expected, but an increasing angle distortion by strain. This has now been proved by X-ray structure analysis of 1 (mp. -70°C) (Fig. 1) and X-X-calculations for 2 (mp. -45°C) (Fig. 2) and 3 (solid at ambient) (Fig. 3), structure previously determined by J. Lawrence, S. G. G. MacDonalds, Acta Cryst. 25, 978 (1969). The angle deformations of 2 and 3 are reflected in the shift of the density maxima, shown in Fig. 2 and 3 (lines drawn with 0.025e/Å<sup>3</sup> heights, negative dotted, 0.5e/Å<sup>3</sup>). Data collections at -170°C, 2θ<sub>max</sub> = 90°, Mo-Kα, Standard dev. 0.001 Å and 0.1° for 2 and 3, 0.002 Å and 0.2° for 1.

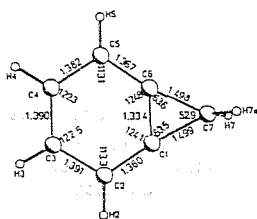


Fig. 1

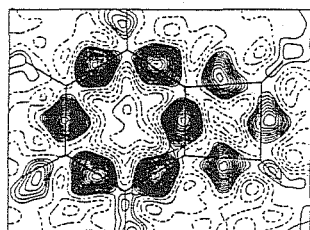
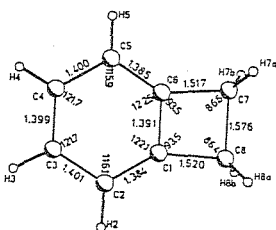


Fig. 2

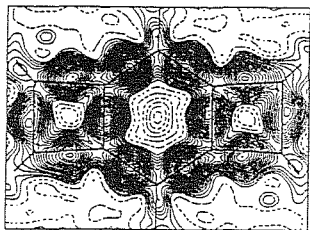
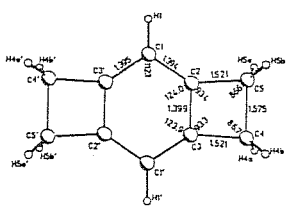
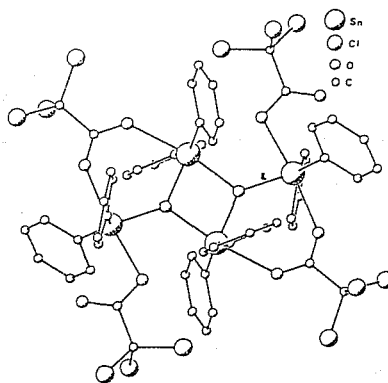


Fig. 3

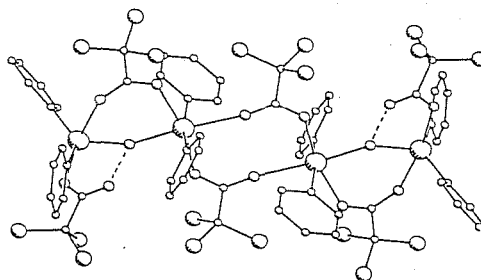
09.1-5 TO BRIDGE OR NOT TO BRIDGE: THE FORMATION OF μ-OXO AND HYDROXO COMPLEXES BY DIPHENYL TIN CARBOXYLATES. By N.W.Alcock and S.M.Roe, Department of Chemistry, University of Warwick, Coventry, CV32 5EU England

An unexpected de-arylation reaction of Ph<sub>3</sub>SnOH with Cl<sub>3</sub>CCOOH leads to the tetrameric μ-oxo species (Ph<sub>2</sub>Sn(O<sub>2</sub>CCl<sub>3</sub>)<sub>4</sub>O<sub>2</sub> (I), rather than the monomer, Ph<sub>2</sub>Sn(O<sub>2</sub>CCl<sub>3</sub>)<sub>2</sub>.



(I)

The reaction of Ph<sub>2</sub>SnO with Cl<sub>3</sub>CCOOH gives a μ-hydroxo species, (Ph<sub>2</sub>Sn(O<sub>2</sub>CCl<sub>3</sub>)<sub>6</sub>(OH)<sub>2</sub> (II).



(II)

Both species contain a mixture of bridging and terminal carboxylate groups. The terminal groups in (II) form internal H-bonds to the μ-hydroxo atom. The conditions for interconversion of these species and the parent monomer have been investigated. Their formation can be correlated with the similar μ-oxo complexes of Iodine(III) and Tellurium(IV) with acids, e.g. [PhI(ONO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>O and [Ph<sub>2</sub>Te(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>O (Alcock & Countryman, J.C.S.Dalton, 1979,851; Alcock, Harrison & Howes, J.C.S.Dalton, 1984,1709).