[2,2]PARACYCLOPHANE – STRUCTURE RESOLVED

The structure of [2,2]paracyclophane **1** has been somewhat controversial for some time. Early x-ray structures indicated that the molecule was quite symmetric, D_{2h} with the phenyl rings and the ethyl bridges eclipsed. Subsequent low-T experiments suggested a lower symmetry form D_2 with a twist that relieves some of the unfavorable eclipsing interactions in the ethano bridges. High-level computations by Grimme[1] and then some by myself[2] indicated that the D_2 structure is the lowest energy conformation, with however a low barrier through the D_{2h} structure.

The suggestion of the D_2 minimum was vehemently criticized by Dodziuk, et al. on the basis of NMR analysis.[3]

Now, a low temperature x-ray experiment of **1** brings clarity to the situation.[4] (The introduction provides a nice summary of the previous 70 year history regarding the structure of **1**.) At temperatures below 45 K, **1** is found as a single structure of D_2 symmetry (with space group *P4n2*). The structure is shown in Figure 1. A phase change occurs at about 45 K, and above 60 K the crystal has $P4_2/mnm$ symmetry.

The structure of **1** at the high temperature appears as D_{2h} with somewhat broader thermal motion of the ethano carbons than the phenyl carbons. The low T structure is in excellent accord with the previous theoretical studies, and the phase transition helps bring into accord all of the previous x-ray crystallographic work.

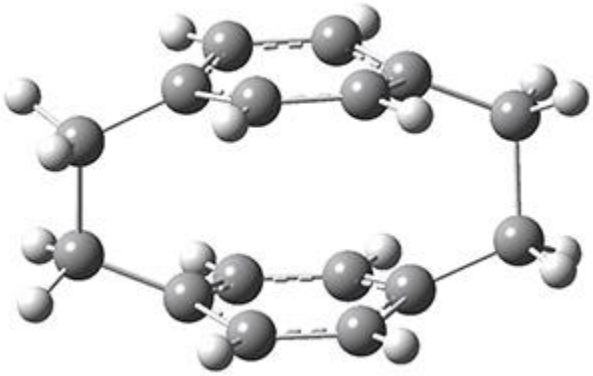

Figure 1. X-ray structure at 15K of **1**.

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