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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIMETHYL-3,8-HEPTALENE-DICARBOXYLATE

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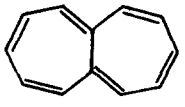
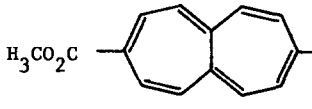
The structure of the 12 π-electron system heptalene (1)has been an object of numerous theoretical studies[1]. To get some information about the geometry of 1 we determined the structure of dimethyl-3,8-heptalene-dicarboxylate (2), synthesized by Vogel and Hogrefe[2]. This structure, with the ester groups in opposite positions, should be more similar to the parent hydrocarbon than the earlier analyzed dimethyl-1,2-heptalene-dicarboxylate (3)[3].



1



2

Crystal data: redbrown orthorhombic flat needles, m.p. 142 - 143° C, recrystallized from ether, $C_{16}O_4H_{14}$, M = 270.3, a = 45.65±0.02, b = 14.65 ± 0.01, c = 3.93±0.005 Å, V = 2628.3 Å^3, Z = 8, d_{exp} = 1.37 gcm^{-3}, d_X = 1.366gcm^{-3}, space group Fdd2.

675 reflections hk0 - hk2 ($2\theta \leq 120^\circ$) were measured with $Cu_{K\alpha}$ radiation (λ = 1.5418 Å) on a two-circle diffractometer. 403 reflections with $|F| \geq 2\sigma_F$ were used for structure determination and refinement. The structure was solved by direct methods and refined to R = 0.065[4].

The molecule has C_2 symmetry and lies on a crystallographic C_2 axis. The bi-

cyclic system is non-planar but consists of two boat shaped 7-membered rings The smaller steric hindrance in 2 compared with 3 leads to flatter 7-membered rings and a less pronounced double bond fixation. From these results it seems possible that heptalene itself is planar or nearly planar.

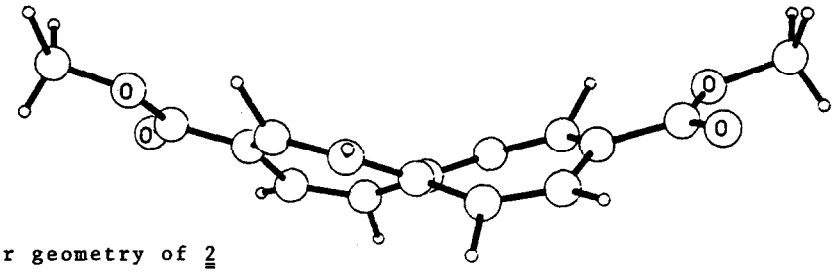


fig. 1: Molecular geometry of 2

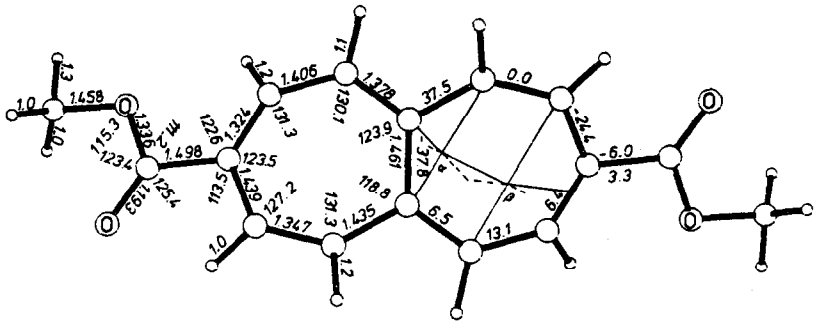


fig. 2: Structure data of 2, left part: bond lengths in Å and bond angles, standard deviations: σ_r = 0.005 Å, σ_α = 0.2°; right part: dihedral angles and structure angles α = 21.1°, ß = 7.5° of the 7-membered rings.

LITERATURE

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