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1,4,7,10-TETRAMETHYL-5,6-DIDEHYDRODIBENZO[a,e]CYCLOOCTENE

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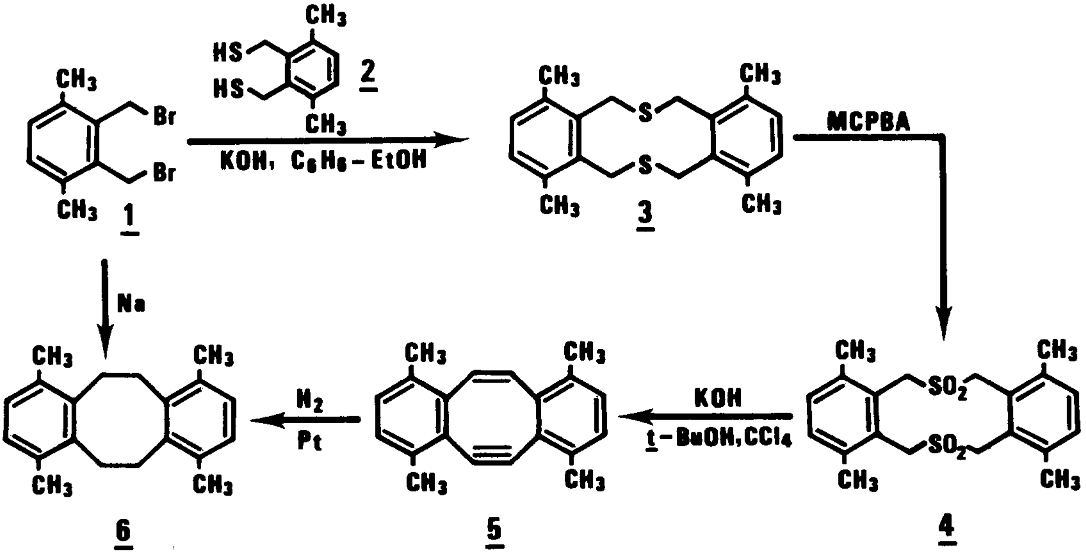
We report the synthesis and structural characterization of the title compound (5), the first known derivative of the intriguing dibenz-annelated planar conjugated eight-membered ring system[1]. Unlike its parent compound, hydrocarbon 5 was found to be thermally stable, undergoing no detectable decomposition at room temperature for periods up to several months.

Reaction of 2,3-bis(bromomethyl)-*p*-xylene (1) with 2,3-bis(mercaptomethyl)-*p*-xylene (2) in the presence of KOH in benzene-ethanol gave 1,4,8,11-tetramethyl-5,7,12,14-tetrahydrodibenzo[c,h][1,6]dithiecine (3)[2], m.p. 218-220°, in 60% yield. Oxidation



with *m*-chloroperbenzoic acid quantitatively converted 3 into the highly insoluble bissulfone 4. Treatment of 4 with powdered KOH in *t*-BuOH-CCl_4[3,4] at room temperature followed by continuous extraction with ether and chromatography on Al_2O_3 (Woelm, neutral, grade I) afforded 5 in 6% yield.

Hydrocarbon 5 formed yellow prisms, which melted with decomposition at 254-255°. The electronic spectrum (n-hexane), which agreed well with that reported for 5,6-didehydrodibenzo[a,e]cyclooctene[1], showed absorptions at 223 sh (ε 16,100), 230 sh (13,900), 249 sh (11,600), 274 (66,300), 282 (95,700), 294 (28,500), 307 (38,800), 355 (3,400), 375 (3,500) and 395 nm (3,980). The nmr spectrum[5] ($CDCl_3$) exhibited two singlets for the aryl methyl protons at τ 7.87 (3H) and 7.61 (3H), a singlet for the olefinic protons at τ 3.50 (1H), and unresolved peaks for the benzenoid protons at τ 3.11-3.20 (2H). The structure of 5 was established by these spectral data, the mass spectrum (M^+ 258) and the elemental analysis (Found: C, 92.90; H, 7.17. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02). The structure of 5 was further supported by conversion into 1,4,7,10-tetramethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (6). Hydrogenation of 5 in EtOAc over Pt gave a mixture from which 6 was obtained by column chromatography. Compound 6 [m.p. 148-150°; nmr (CCl_4), τ 7.81 (3H, s, $ArCH_3$), 6.97 (2H, s, $ArCH_2$) and 3.37 (1H, s, ArH); M^+ 264; elemental analysis, Found: C, 91.02; H, 9.27. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15.] was identical in all respects to a sample independently prepared by the Wurtz reaction of 1.

Final confirmation of structure 5 was provided by X-ray crystallography. Compound 5 crystallizes in space group $P2_1$, with lattice parameters a = 10.884(2), b = 13.290(3), c = 4.965(1) Å and β = 95.42(2)°. There are two molecules per unit cell. Reflections $h0\ell$ with $(h+\ell)$ odd are either very weak or absent. The intensities of 992 independent reflections up to $\sin\Theta/\lambda = 0.538$ were measured in the Θ-2Θ scan mode on an automated diffractometer using monochromatized Cu-$K\alpha$ radiation.

To a very good approximation, the space group was taken as $P2_1/n$ in accordance with a disordered structure in which the molecule possesses an apparent centre of symmetry. In this model, each molecule has two possible orientations, one being related to the other by the interchange of the ethylenic and acetylenic bridges; the two molecular orientations are assumed to occur randomly throughout the crystal lattice. The structure was solved with MULTAN[6]. All ten C atoms in the asymmetric unit (Fig. 1) were located in the E-map. Full-matrix anisotropic least-squares refinement yielded a final $\underline{R}$ of 0.113 for 761 observed reflections. The function minimized was $\sum\underline{w}(|F_o|-|F_c|)^2$, with $\underline{w} = (8.0 + |F_o| + |F_o|^2/125.0)^{-1}$. A Fourier map showed that the electron densities around the bridging carbon atoms C(9) and C(10) were very diffuse. Further refinement in the true space group $\underline{P}2_1$ did not prove successful due to the small number of weak $\underline{h}0\ell$ reflections with $(\underline{h}+\ell)$ odd.

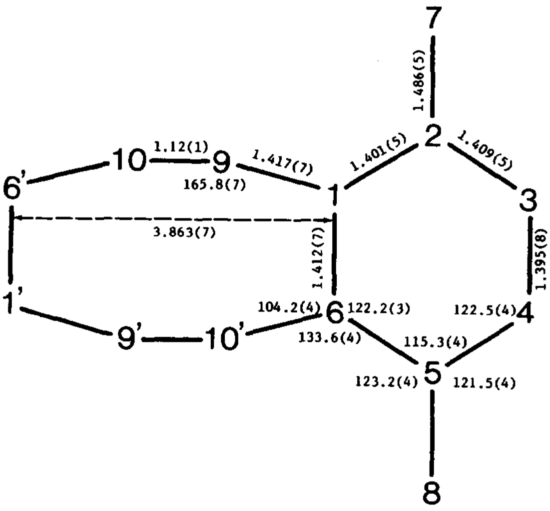


Fig. 1. Molecular dimensions and numbering scheme of 5. Primed and unprimed atoms are related by the centre of symmetry at the molecular centre.

The mean values of the measured bond distances and angles, with molecular symmetry mmm (D_{2h}) assumed, are shown in Fig. 1. The molecule is planar within experimental error. The central eight-membered ring has a span of 3.863(7) Å which is, as expected, significantly longer than the corresponding bridging distance of 3.834(3) Å in 5,6,11,12-tetradehydrodibenzo[a,e]cyclooctene[7].

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References and Notes

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