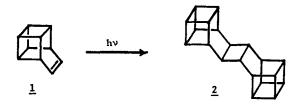
SYNTHESIS AND STRUCTURE OF BASKETENE PHOTODIMER, C20H20

N. J. Jones, W. D. Deadman and E. LeGoff¹ Department of Chemistry, Michigan State University East Lansing, Michigan, 48823

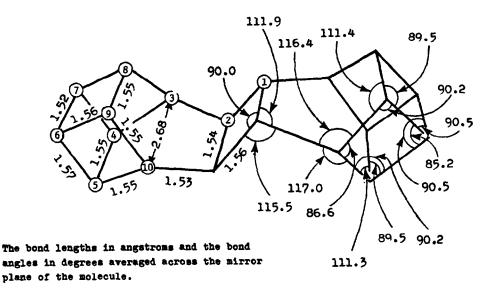
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In a photochemical reaction not unlike that of other strained ring unconjugated olefins basketene, <u>1</u>, undergoes cycloaddition to itself forming a dimer, $C_{20}H_{20}$. While the chemical and physical properties are consistent with a $2\pi + 2\pi$ photodimerization forming a highly strained system such as 2 together they were sufficiently ambiguous so as not to exclude other dimers.



To establish the structure an x-ray crystallographic study was undertaken.

The crystals of $C_{20}H_{20}$ were triclinic, space group P1, with: a = 10.089 (4), b = 6.529 (3), c = 5.450 (3) Å; α = 115.20 (5), β = 103.11 (5), γ = 76.35 (5)°; d_{obsd} = 1.36, d_{calcd} = 1.38 g cm⁻¹; z = 1. A total of 644 independent reflections was measured on a General Electric XRD-5 diffractometer with Cu K_a radiation (20 \leq 100°). The structure was solved by a combination of symbolic addition and Patterson methods. Hydrogens were located from a difference Fourier calculation. The final R is 8.6%. The average carbon-carbon bond length is 1.55 Å; and the average carbon-hydrogen length is 1.07 Å, exactly the values found for cubane². Furthermore, the bond lengths and angles of <u>2</u> agree well with those reported for basketane-9-ol p-bromobenzoate³ and basketane-9,10-dicarboxylic acid⁴. C-C-H angles in <u>2</u> are within the range of 105° to 127° (σ = 5°) with two exceptions. These are angle C(7)-C(6)-H(6) and angle C(6)-C(7)-H(7) both of which are 135°. Many of the other bond lengths and angles which involve C(6) and C(7) are also anomalous reflecting a change of hybridization from the normal sp³.



Synthesis of 2: A 5.6-molar solution of $\underline{1}$ in reagent acetone was irradiated for 24 hours with a Hanovia 450 watt lamp (Pyrex filter). Crystals slowly formed. These were collected, washed with acetone and dried to give $\underline{2}$ (27% yield). Analytically pure $\underline{2}$ is obtained by sublimation (130°/0.1 mm) or recrystallization from heptane; mp 248-250°; C, 92.30; H, 7.73; m/e (rel. inten.); 260.1559 (4.01), 130.0770 (39.56), 129.0697 (100.00), 128.0622 (68.28); IR(KBr): 2960, 2900, 1323, 1266, 1225, 1202, 930, 862, 775, 765 cm⁻¹; Raman 2995, 2915, 995, 935, 865, 305 cm⁻¹.

Attempts to reorganize $\underline{2}$ to form the symmetrical $C_{20}H_{20}$ hydrocarbon, dodecahedrane, using a variety of Lewis acid catalysts has thus far been unsuccessful. The mair products from these reactions are light colored aluminum containing polymeric materials.

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References

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