

eq 3 leads to eq 5, which predicts a linear relationship between

$$\frac{1}{\Delta\phi_f} = \frac{1}{\phi_f^C - \phi_f^S} \left(1 + \frac{S_0 + K_d^*}{nA_0} \right) \quad (5)$$

the reciprocals of $\Delta\phi_f$ and A . Reasonable plots were obtained for all three of the surfactant stilbenes; values for K_d^* and α , the degree of complex formation, as listed in Table I, were extrapolated from these plots.³⁰

The trans \rightarrow cis photoisomerization of S_6 was also investigated in the presence and absence of amylose. As might be anticipated from the enhancement of fluorescence, the isomerization was retarded by addition of amylose. It was found, for example, that at $A_0 = 7.21 \times 10^{-5}$ M the $\phi_{\text{trans}}^{\text{obsd}}$ for S_6 in the inclusion complex is approximately 0.22 or about 44% of that in homogeneous Me_2SO -water.

These results reveal several features of the amylose inclusion complexes. First of all, the extrapolated values for stilbene fluorescence yields in the complexes, $\phi_f^C \approx 0.230$ (for S_4 and S_6) and $\phi_{\text{trans}}^C = 0.22$ are very similar to those obtained for these and other surfactant stilbenes incorporated into various bilayer vesicles below or near the phase-transition temperature.²² These values indicate a reasonably restricted environment for the stilbene chromophore or a relatively high effective "microviscosity" in the amylose complexes. The similarity to results obtained with vesicles is interesting since the microstructures of the two assemblies must be quite different. The amylose has the glucopyranose units in the C1 chair conformation³¹ and can form helical cavities (6-helix, 7-helix) with approximate internal diameters of 4.5 and 7.0 Å, respectively.^{32,33} The cross-sectional areas for the helical cavities are 16 and 38 Å², respectively. The 6-helix is the most stable form and apparently the cavity used for incorporation of benzene and several aliphatic derivatives; however, the flexibility of the amylose is such that larger cavities can be formed to accommodate somewhat larger molecules.³² The cavity size for the 6-helix is somewhat smaller than the indicated cross-sectional area for the S_n compounds—20–22 Å² in compressed monolayer films at the air-water interface.²² In the latter phase photoisomerization of the stilbenes is virtually eliminated. Thus the present results suggest that the stilbene chromophore may exist in a cavity somewhat between a 6-helix and 7-helix in which molecular motion is restricted but not prohibited to the extent in condensed monolayers or crystals.

The relatively high sensitivity of the fluorescence of stilbene S_4 , S_6 , and S_{12} to complex formation suggests that these or similar probes can be useful to measure amylose binding constants for nonfluorescence molecules or even molecules without a characteristic chromophore. Indeed this is the case; we find addition of several surfactants results in a decrease in the stilbene fluorescence, presumably due to competitive binding to the amylose.

That formation of the amylose inclusion complexes is governed largely by hydrophobic effects is indicated by the pronounced variation in dissociation constants K_d^* , observed for the different stilbene derivatives. Thus stilbene does not form a detectable complex in the concentration ranges employed while the surfactant stilbenes complex with decrease in K_d^* paralleling increase in hydrophobicity. As shown in Table I, there is a reasonable correlation for the surfactant stilbenes between $-\Delta G$ and the effective number of methylene groups; similar incremental

(29) Although it is true that for S_{12} , the term $CS \approx C^2$, for each of the surfactant stilbenes, analysis of the data in Table I confirms that the term C^2 is negligible compared with the other terms in the expansion developed from eq 2.

(30) By use of the σ -C (surface tension-concentration of substrate) curve, the n value can be determined experimentally. In the present case, n values were calculated from the DP of amylose used and the lengths of surfactant stilbenes based on the previous data presented in ref 12.

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$-\Delta G/\text{CH}_2$ values have been observed for quite different molecules such as carboxylic esters of *p*-nitrophenol, suggesting that this may be a fairly general phenomenon.¹³

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Synthesis and Structure of 8-Carboxy[6]paracyclophane

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Central to the interest in the chemistry of $[n]$ paracyclophanes with small bridges ($n = 6^1$ or 7^2) is the distortion of the aromatic ring from planarity and the effect of the distortion on its physical and chemical properties. The smallest $[n]$ paracyclophane thus far obtained has been the [6] isomer, first reported by Jones et al. in 1974.^{1a} However, the crystal structure determination of this system has not been done due to the inaccessibility of either the parent hydrocarbon or suitable derivatives. We report herein the novel and efficient synthesis and single-crystal X-ray structure determination of 8-carboxy[6]paracyclophane (**2**), which has, to our knowledge, the most highly deformed benzene ring ($\alpha_{\text{av}} = 20.7^\circ$, $\beta_{\text{av}} = 18.8^\circ$) obtained to date.

The synthesis of **2** takes advantage of the facility of Dewar benzene \rightarrow benzene valence isomerization of [6.2.2]propelladiene to [6]paracyclophane^{1b} (Scheme I). Ring contraction of the propellanone **3**,³ prepared from the bicyclic α,β -unsaturated ketone, by employing photo-Wolff rearrangement of the α -diazo ketone derived from **3** in methanol afforded a mixture of two epimeric [6.2.2]propellanes, **4X** and **4N** (**4X/4N** = 2), in 47% yield. Treatment of either **4X** or **4N** with LDA/diphenyl diselenide at -70°C furnished a mixture of two isomeric α -selenides, **5X** and **5N** (**5X/5N** = 6–10), in 89% yield. Oxidation of the major isomer **5X** in dichloromethane with H_2O_2 at room temperature yielded the propelladiene **6** in 72% yield. Valence isomerization of **6** took place smoothly at 60°C leading to the formation of the cyclophane **1** quantitatively. Hydrolysis of **1** gave the crystalline **2**, mp 123 – 125°C , in 87% yield.

A single-crystal X-ray analysis of **2** gave precise information about the deformation of the benzene ring of the [6]paracyclophane system.^{4,7} Figure 1 is an ORTEP drawing⁸ of **2**. The

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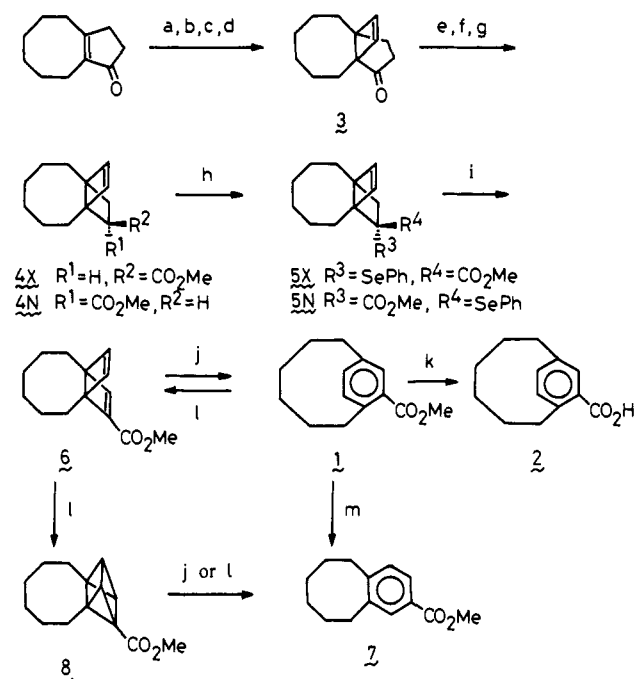
(1) (a) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815. (c) Liebe, J.; Wolff, C.; Tochtermann, W. *Tetrahedron Lett.* **1982**, *23*, 171; (d) **1982**, *23*, 1143; (e) **1982**, *23*, 2439.

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(3) All new compounds showed satisfactory spectral properties. Satisfactory elemental analyses were obtained on all new compounds except for **6** and **8**, which are readily converted to **1** and **7**, respectively. Details are recorded in the supplementary material.

(4) Crystal data of **2**: $\text{C}_{12}\text{H}_{16}\text{O}_2$, M_r 204.3, tetragonal, space group $P4_2/n$, $a = 16.646$ (1) Å, $c = 7.987$ (1) Å, $U = 2213.3$ (3) Å³, $D_x = 1.226$ g cm⁻³, $Z = 8$. Intensity measurements were made on a Rigaku four-circle diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation. A total of 1395 reflections was collected up to $2\theta = 110^\circ$, among which 1185 were nonzero reflections. The structure was solved by the direct method (MULTAN-78)⁵ and refined by the block-diagonal least squares (HBL5-V)⁶ to the R index of 0.123 (non-hydrogen atoms anisotropically, hydrogen atoms of benzene ring isotropically). The fractional atomic parameters are listed in Table S1.

Scheme I



^a Dichloroethylene (cis-trans mixture), $h\nu$, Pyrex.
^b $HOCH_2CH_2OH, H_2SO_4, C_6H_6$. ^c Na, NH_3, Et_2O . ^d $1.2 N HCl, Et_2O$. ^e $HCO_2Et, EtONa, Et_2O$. ^f TsN_3, Et_3N, CH_2Cl_2 . ^g $h\nu$, Pyrex, MeOH. ^h LDA, Ph_2Se_2, THF . ⁱ $H_2O_2, pyridine, CH_2Cl_2$.
^j Heat. ^k $KOH, MeOH$. ^l $h\nu$, Pyrex, hexane. ^m $h\nu$, quartz, hexane.

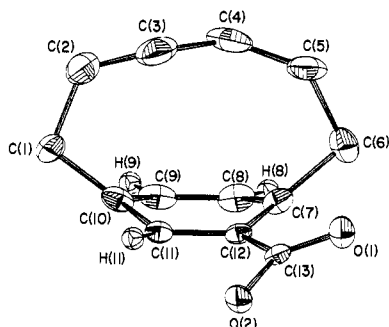


Figure 1. Molecular structure of **2**. Non-hydrogen atoms are drawn by the thermal ellipsoids at the 20% probability level. Hydrogen atoms are shown by the spheres corresponding to the artificial isotropic temperature factor of 1.0 \AA^{-2} .

most remarkable structural feature of **2** is, of course, the distortion of the benzene ring from planarity: the para carbons (C(7) and C(10)) are lifted out of the plane of the other four benzene carbons (C(8), C(9), C(11), and C(12)) by 21.1 and 20.3°, respectively. The benzyl carbons (C(1) and C(6)) are out of the planes of C(9)-C(10)-C(11) and C(8)-C(7)-C(12) by 17.4 and 20.2°, respectively. Comparison of these values with those of 3-carboxy[7]paracyclophane ($\alpha_{av} = 16.8^\circ, \beta_{av} = 6.8^\circ$)^{2b} clearly indicates that the out-of-plane deformation, especially that of the benzyl carbons, is significantly greater in the smaller bridged compound. Moreover, the bond angles of the side chain (C(2),

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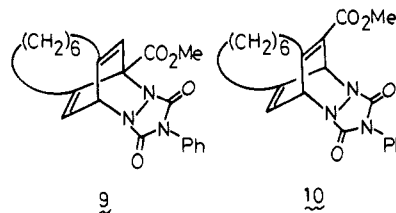
(7) In order to obtain more detailed information on the structure of the bridging chain, a low-temperature structure determination is now being performed, and the results will be published elsewhere.

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C(3), C(4), C(5)) are considerably widened from the normal $C(sp^3)-C(sp^3)-C(sp^3)$ bond angle (average 126.5°), even if one takes into account the inaccuracy of the data due to the thermal motion of the bridge.⁷

Interestingly, it was found that the photochemical valence isomerization of **1** takes place stepwise in the sequence **1** → **6** → **8** → **7** (Scheme I): irradiation of a hexane solution of **1** with a high-pressure mercury lamp in a quartz vessel gave the benzocyclooctene **7** in 47% isolated yield as a single product. Irradiation through a Pyrex filter, however, led to rapid formation of the Dewar isomer **6**. When irradiation of **6** was continued under the above conditions, slow conversion to the prismane derivative **8** was observed. Further irradiation of **8** furnished **7**.

Furthermore, treatment of **1** with a dienophile such as *N*-phenyl-1,2,4-triazoline-3,5-dione afforded two kinds of [4 + 2] cycloadducts, **9** and **10**, in a ratio of 1:2. The details will be reported shortly.



Registry No. 1, 84538-15-8; **2**, 84538-16-9; **3**, 84538-10-3; α -diazio-3, 84538-11-4; **4X**, 84538-12-5; **4N**, 84620-30-4; **5X**, 84538-13-6; **5N**, 84620-31-5; **6**, 84538-14-7; Ph_2Se_2 , 1666-13-3; *cis*-dichloroethylene, 156-59-2; *trans*-dichloroethylene, 156-60-5; 2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopentacycloocten-1-one, 38262-50-9.

Supplementary Material Available: Listing of the spectral and analytical data of new compounds and Table S1 listing the fractional atomic coordinates (6 pages). Ordering information is given on any current masthead page.

Isolable Species from Nucleophilic Attack at Sulfinyl and Sulfonyl Sulfur: A Sulfurandioxide (10-S-5)¹ Salt and a Sulfuranoxide (10-S-4)¹ Salt

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Mechanisms of nucleophilic attack at sulfinyl² and at sulfonyl³ sulfur have been exhaustively studied. Evidence has been sought to support a choice between (a) a two-step process, via sulfurane intermediates, and (b) a one-step concerted (S_N2) process. A recent review⁴ has championed the first mechanism, a, to explain

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