

CYCLOPHANES V. anti-[2.2](2,6)AZULENOPHANE.

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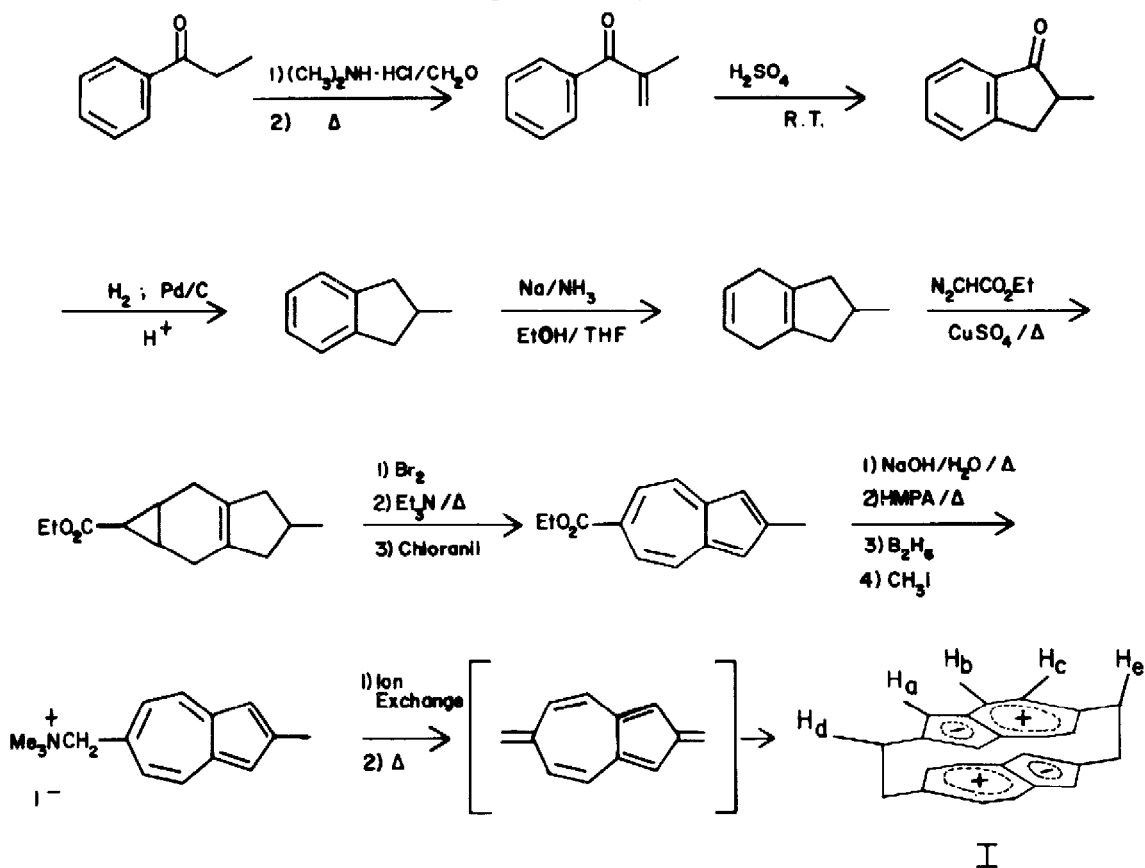
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During the past years a number of publications have appeared concerning charge-transfer interactions between aromatic groups within cyclophanes.¹ Our interest in intramolecular charge-transfer processes and semi-conduction in solely carbonaceous materials led us to consider the potential interactions that the strongly polarized azulene nucleus would have within a cyclophane macrocycle. We wish to report on a successful synthesis of the title compound, the first phane incorporating two azulene residues.²

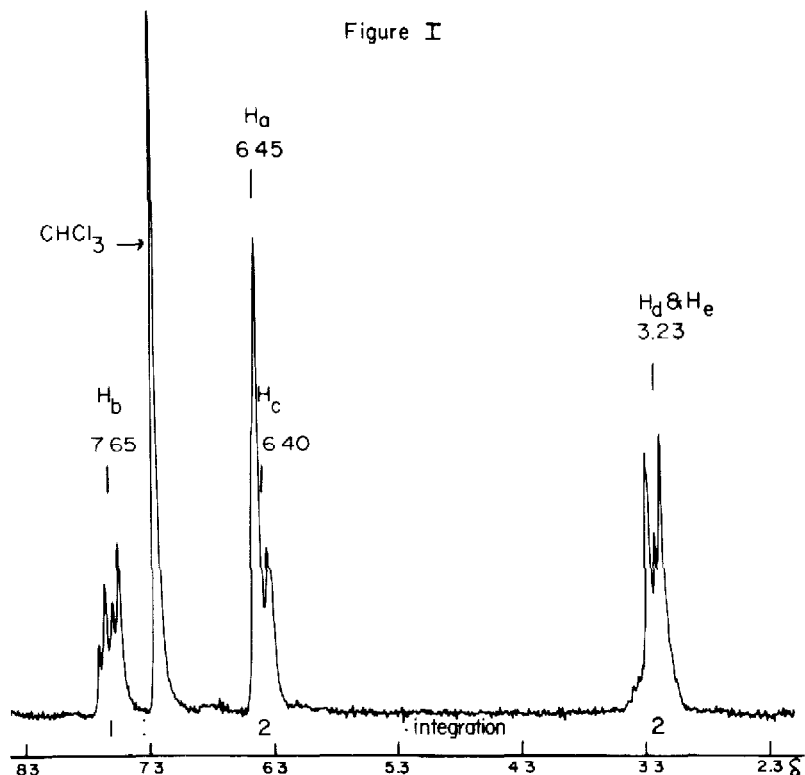
Scheme I



The synthesis is described in Scheme I and will be discussed in detail in a full paper. All reactions except for the last one gave products in greater than 50% yield and all new compounds³ were accurately characterized by spectral and combustion (within 0.4%) analysis. The Hofmann pyrolysis afforded the title compound I in 6% yield after repeated chromatographies on silica gel and crystallization from CHCl_3 . At least three other monomeric products were identified but none corresponded to the syn-isomer of I in which the negative end of the dipoles of both azulene moieties are oriented in the same direction. Compound I is blue-green in color and does not melt up to 340°C suggesting a highly symmetrical structure.

The structural assignment for I is based on spectral evidence. The mass spectrum shows two prominent peaks; a molecular ion at m/e 308.155 (Calcd. for $\text{C}_{24}\text{H}_{20}$ m/e 308.156) and a base peak at m/e 154 associated with cleavage of the two ethylene bridges. This fragmentation pattern is normally observed in [2.2]phanes⁴ and is consistent with either the syn- or anti-structure of I. The infrared spectrum is simple showing absorptions at 3080-2850, 1568, 1400 cm^{-1} characteristic of the azulene nuclei.⁵

The nmr spectrum⁶ is reproduced in Figure I and is consistent with a cyclophane structure and the anti-orientation of the azulene rings in I. The chemical shift for the a, b and c protons of the azulene rings are found respectively at 0.69, 0.43 and 0.67 ppm upfield relative to those in 2,6-dimethylazulene.⁷ These upfield shifts are expected due to the position of protons relative to the shielding cone of the proximate azulene ring. The upfield shift of the a and c



protons compares favorably with the 0.68 ppm upfield shift observed for the benzenoid protons in [2.2]paracyclophane relative to those of p-xylene.⁸ The smaller upfield shift of the b protons is characteristic of their being further removed from the shielding region of the proximate azulene ring (see Figure II), and thus are shielded less than the a and c protons. This smaller upfield shift of the

b relative to the a and c protons is consistent with the anti-structure for I since the b protons in the syn-isomer would be expected to exhibit similar upfield shifts as protons a and c due to their similar proximity to the shielding region of the neighboring azulene ring. In addition to the upfield shift exhibited for the azulenoid protons in I there is also observed a downfield shift of 0.53 ppm of the bridge d and e protons relative to the methyl protons in 2,6-dimethyl azulene.⁷ The multiplicity of the absorption for these bridge protons also substantiates the anti-orientation of the azulene rings in I since they would be expected to show an AA'BB' pattern. In contrast, the syn-isomer should exhibit a singlet for each of the two equivalent sets of protons adjacent to the five and seven membered fused portions of the azulene rings. This is not observed.

Finally the electronic spectrum of I is consistent with a cyclophane structure and exhibits two broadend maxima; one in the visible region at $\lambda_{\text{max}}^{\text{CHCl}_3}$ 605 nm, $\epsilon = 418$ and the other in the ultraviolet region at $\lambda_{\text{max}}^{\text{CHCl}_3}$ 277 nm, $\epsilon = 69,700$. Similar to the electronic spectra of other [2.2]phanes⁹ there is observed a general broadening of all bands in the spectrum and a bathochromic shift of 55 nm of the long wavelength band relative to 2,6-dimethylazulene.¹⁰ The short wavelength band is hypsochromically shifted by 8 nm relative to that of 2,6-dimethylazulene¹⁰ and since it is a higher energy absorption is indicative of an attractive π - π interaction between the two azulene rings.⁹

We are presently studying the physical properties¹¹ of this interesting molecule and have observed by electronic spectroscopy mono- and di-protonated forms of I when treated with trifluoroacetic acid. A charge transfer band is observed in the mono-protonated form and may also be present in the parent phane but is masked by the visible absorption. Details of the syntheses and properties of this unusual molecule will be published shortly in a full paper.

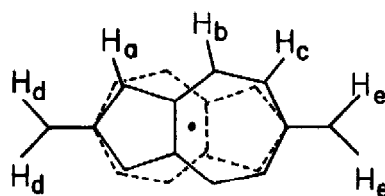


Figure II
Anti-orientation of I. For syn-isomer rotate top ring by 180°.

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References

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2. [8] (1,3)Azulenophanes have been synthesized, see, A. G. Anderson, Jr. and R. D. Breazeale, *J. Org. Chem.*, 34, 2375 (1969).
3. Evidence confirming the 2,6- substitution pattern on the azulene nucleus was obtained by spectral and mp comparisons of the acid (mp 250°) formed on hydrolysis of the methyl-carbethoxy azulene synthesized in Scheme I with known 2-methyl-6-carboxyazulene (mp 251°; Pl. A. Plattner, A. Fürst, A. Müller and A. Somerville, *Helv. Chim. Acta.*, 34, 971 (1951)).
4. a) Philip M. Keehn, Ph.D. Thesis, Yale University, 1969; b) Hans J. Reich and Donald J. Cram, *J. Amer. Chem. Soc.*, 91, 3534 (1969).
5. "Non-Benzenoid Aromatic Compounds", David Ginsberg Ed., Interscience Publisher, Inc., N.Y. 1959; Chapter V, "Azulenes", by E. Heilbronner.
6. NMR spectra were taken on a Bruker WH-90 Fourier Transform Spectrometer.
7. The nmr spectrum of 2,6-dimethylazulene is as follows: 8.07 δ , d, 2H; 7.14 δ , s, 2H; 7.07 δ , d, 2H; 2.78 δ , s, 3H; 2.75 δ , s, 3H.
8. D. J. Cram, C. K. Dalton and G. R. Knox, *J. Amer. Chem. Soc.*, 85, 1088 (1963).
9. D. J. Cram, N. L. Allinger and H. Steinberg, *J. Amer. Chem. Soc.*, 76, 6132 (1954).
10. The electronic spectrum of 2,6-dimethylazulene is as follows: vis- $\lambda_{\text{max}}^{\text{CHCl}_3}$ 550 nm, $\epsilon = 249$, sh at λ 652, 585 and 512 nm; uv - $\lambda_{\text{max}}^{\text{CHCl}_3}$ 290 nm. $\epsilon = 58,250$ and 280.5 nm, $\epsilon = 47,200$ sh at λ 350, 335 and 307 nm.
11. A single crystal structure determination is presently being carried out by Professor Bruce Foxman.