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SYNTHESIS AND CHARACTERIZATION OF ANTI-[2.2](1,6)AZULENOPHANE

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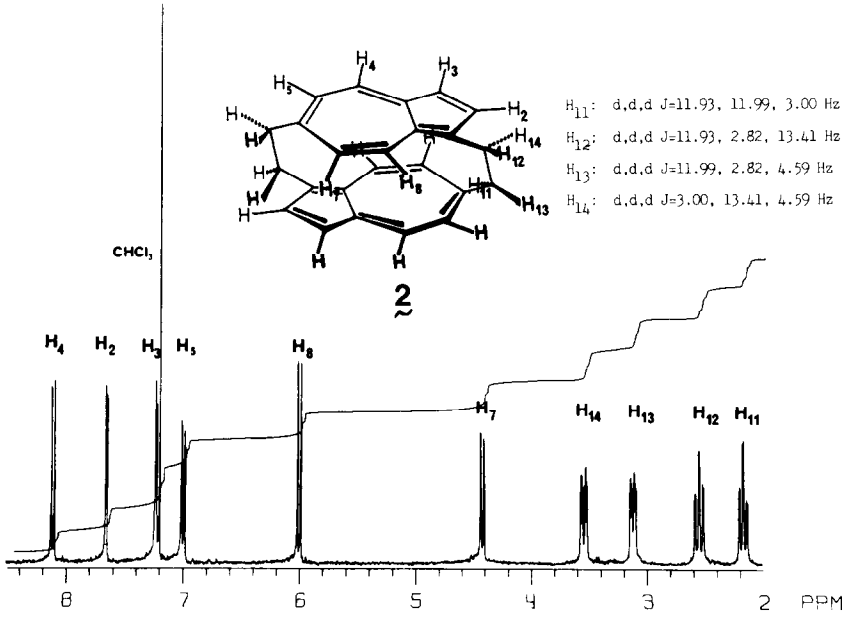
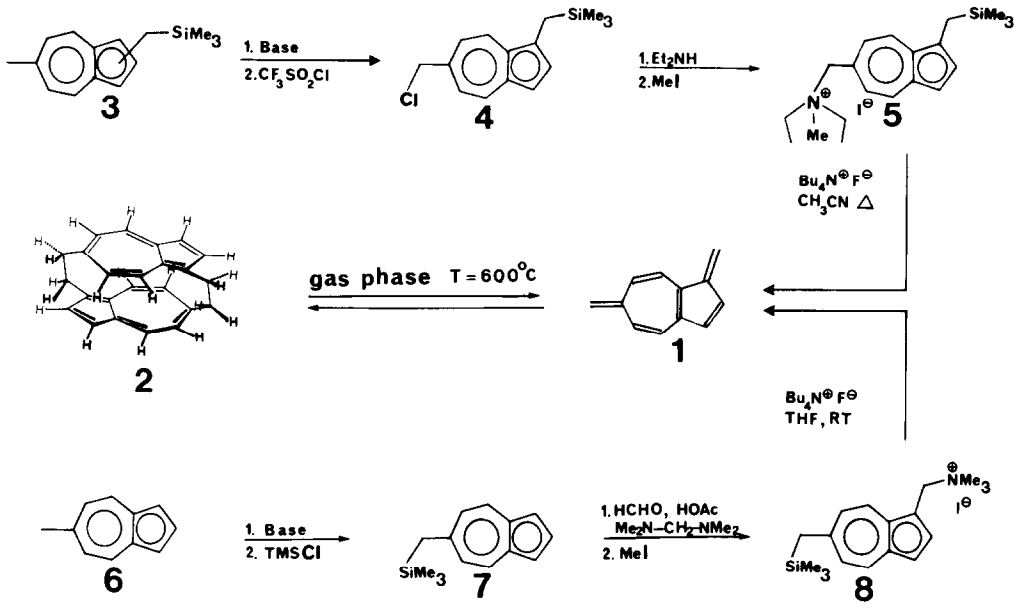
ABSTRACT: Two synthetic pathways affording anti-[2.2](1,6)azulenophane via fluoride induced 1,8 elimination from trimethylsilyl-tetraalkylammonium salts are described. Spectral data are reported that allow the structural assignment for the title compound.

1,6-Azulylene (1) is one of a family of unstable polyenes which has not been previously characterized. Elucidation of the interesting features of the electronic states[1] of this reactive species requires an efficient synthesis of an appropriate precursor. The hitherto unknown anti-[2.2](1,6)azulenophane (2) is an obvious[2] possibility for this purpose and we wish to describe two short pathways each affording the title compound (as a single isomer[3]), by 1,8 elimination from a trimethylsilyl-tetraalkylammonium salt (Scheme I). Spectral data (including ^{1}H-NMR, Figure 1), which establish the structure of the isolated material as the anti configurational isomer (2) and its flash vacuum pyrolysis temperature, are also included.

Figure 1. ^{1}H NMR spectrum (360 MHz) of 2.



Scheme I



Synthesis (Scheme I): Both synthetic routes utilized the Hafner[5] method to obtain 6-methylazulene (6) or its derivatives (3). Lithium (trimethylsilyl)methylcyclopentadienide and N-butyl-4-picolinium bromide afforded a 52% yield of a mixture[6] of the expected 1- and 2-(trimethylsilyl)methyl substituted 6-methylazulenes (3). The 6-chloromethyl derivative (4) was obtained as a single isomer[7] in 46% yield (as a blue oil after careful column chromatography) after treatment of 3 with sodium N-methylanilide in tetrahydrofuran followed by trifluoromethanesulfonyl chloride.[8] Conversion to the desired quaternary ammonium salt[7] (5) was easily accomplished (27% yield) by treatment of 4 with diethylamine followed by methyl iodide. Addition of an equivalent (1.0) of tetrabutylammonium fluoride[9] to a dilute refluxing solution of 6 resulted in a 17% yield of 2 after chromatography.

Alternatively, 2 can be synthesized starting with 6.[5] Treatment of 6-methylazulene (6) with lithium tetramethylpiperidinide and then trimethylsilyl chloride gave 7[7] in 68% yield (blue-purple crystals, m.p. 106-108°C). Aminomethylation at C_1 of 7 was readily accomplished using a slight modification of the procedure of Anderson.[10] Quaternization with methyl iodide gave 8 in 79% yield (from 7).[7] The cyclophane (2) was formed from 8 in 10.4% yield after addition of tetrabutylammonium fluoride to a dilute solution of 8 in tetrahydrofuran at ambient temperature.

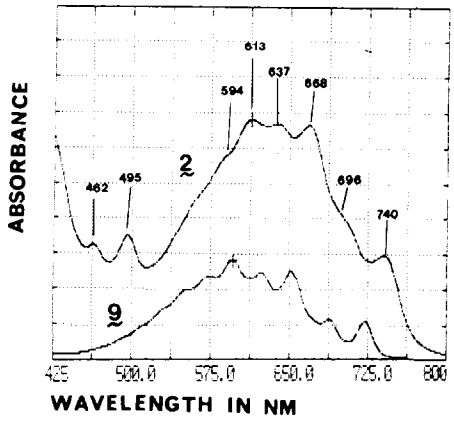
Characterization of 2: Compound 2 is a blue-green solid (m.p. >350°C). The mass spectrum (70 eV) shows a molecular ion peak at m/e 308.156 (calcd. for $C_{24}H_{20}$: m/e 308.156) and a base peak at m/e 154. Figure 1 displays the 360 MHz ^{1}H NMR spectrum of 2 which was the same

for the material obtained from either 5 or 8. The structural assignment of (2) rests on ^{13}C-NMR and ^{1}H-NMR data. The ^{13}C-NMR spectrum shows 10 aromatic carbon resonances (δ (ppm): 151.4, 142.2, 135.7, 135.6, 135.1, 131.8, 128.2, 126.7, 122.9, 115.4; 4 quaternary carbons) and 2 aliphatic resonances (δ (ppm): 45.2 and 31.4) as required for a [2.2](1,6)azulenophane possessing either a C_2 symmetry axis or a center of inversion. All aromatic signals in the ^{1}H-NMR spectrum are split into doublets (Figure 1). These observations confirm 1,6 disubstitution on both of the azulene units.

There are 6 stereoisomers of 2 when both conformations and configurations are considered.[11] Both of the conformational isomers of the [1,1';6,6'] (syn) configurational isomer[11] should display two distinct AA'BB' patterns for the two bridging ethano groups, whereas both of the conformational isomers of [1,6';6,1'] (anti) diastereomer[11] should show first order splitting into a d,d,d for each of the four distinctly nonequivalent methylene hydrogens in the two ethano bridges. The aliphatic part of the ^{1}H-NMR spectrum clearly shows the first order behavior and splitting into d,d,d, establishing that the compound obtained here is one of the conformational isomers of the [1,6';6,1'] (anti) configuration. The aliphatic portion of the ^{1}H-NMR spectrum (2.2-3.8 ppm) can be simulated with the set of coupling constants presented in Figure 1.

The distinction between the two conformations of the [1,6';6,1'] (anti) configurational isomer is possible considering interdeck magnetic anisotropy effects. As indicated in Figure 1, two signals assignable to aromatic protons show large upfield shifts (δ 4.4, 6.0 ppm) compared to 1,6 dimethylazulene (9).[12,13] The positions of the remaining aromatic resonances are within 0.05 ppm of those for the monomeric reference compound (9). The anti conformational isomer (2) is expected to display large upfield shifts for the pair of two (H_7,H_8) proton sets related by the inversion center and negligible small changes in chemical shifts for the remaining aromatic signals. The syn conformational isomer of 2 would be expected to show a large upfield shift of one aromatic signal and moderate shifts for several of the others. Therefore the ^{1}H-NMR data are only compatible with formation of the anti conformational isomer of (2), and it is the only cyclophane isolated from either of the routes of Scheme I.

Figure 2. Visible spectrum of 2 compared to 9.



The uv spectrum of 2 shows absorptions at 257 nm, sh (log ε = 4.4), 275 nm (log ε = 4.7), 301 nm, sh (log ε = 4.3) and 360 nm (log ε = 3.6). The absorptions in the visible region are shown in Figure 2 together with that of 1,6-dimethylazulene (9).[13] A slight bathochromic shift for the longest wavelength absorption and two new bands at 462 nm and 495 nm are observed. Ito and his coworkers[14] have observed an analogous behavior in the case of [2.2](1,3)azulenophane and related the new bands to transannular pi-electron interaction between the azulene moieties. Preliminary results from flash-vacuum-pyrolysis/mass spectrometry suggest that 2 is converted to 1 at 600°C as indicated by the observation of an m/e 154 peak (with no m/e 308 peak) from a stream of 2 passing through a pyrolysis oven attached to a mass spectrometer. The formation of 2 in solution could occur through dimerization of the polyenic intermediate 1 as indicated in Scheme I but alternative possibilities, i.e nucleophilic displacement, could also account for its formation.

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3. 1,8 Hofmann elimination was found to yield a 5:4 mixture of the anti and syn isomers of [2.2](2,6)azulenophane. Kato, N.; Matsunaga, H.; Oeda, S.; Fukazawa, Y.; Ito, S. Tetrahedron Lett. 1979, 2419.

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6. The ratio of 1,6 vs. 2,6 disubstituted azulenes in the mixture designated as 3 was 3:1 as determined by ^{1}H-NMR integration. We were not able to separate this mixture on a preparative scale. Chromatography of the products obtained from chlorination of this mixture did afford 4 as a pure substance.

7. All new compounds gave satisfactory spectral (^{1}H-NMR, IR, MS, UV) and analytical (elemental analysis and/or high resolution MS) data.

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11. There are two configurational isomers, one with ethanobridges connecting the 1,1' and 6,6' positions of the azulene rings (syn-configurational isomers), the other with the bridges connecting the 1,6' and 6,1' positions of the azulene rings (anti-configurational isomer). Each of these two configurational ([1,1';6,6'] and [1,6';6,1']) isomers can exist as either a syn or anti conformation. The anti conformations show a "stepwise structure" for the aromatic planes. The syn (gauch-ethano) conformations feature face-to-face stacking of the aromatic planes. Furthermore, the syn configurational isomer posessing the anti conformation and the anti configurational isomer possessing the syn conformation are dissymmetric and can exist as enantiomers.

12. The ^{1}H-NMR spectrum of 1,6 dimethylazulene is as follows ($CDCl_3$, 100 MHz). δ 8.06 (d, J=9.5 Hz, 2H, $H_{4,8}$); 7.62 (d, J=3.5 Hz, 1H, H_2); 7.23 (d, J=3.5 Hz, 1H, H_3); 6.94 (br. d, J ca. 10 Hz, 2H, $H_{5,7}$); 2.64 (s, 3H); 2.59 (s, 3H).

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