

### AZULENOPHANES III

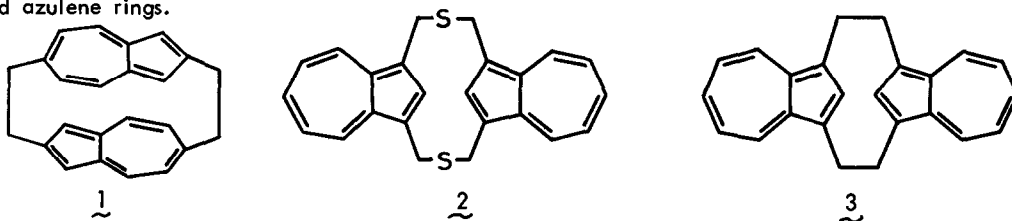
#### SYNTHESES AND PHYSICAL PROPERTIES OF [2.2](1,3)AZULENOPHANE AND 2,13-DITHIA[3.3](1,3)-AZULENOPHANE

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In the course of our studies on [2.2]phanes incorporated with nonbenzenoid aromatic rings, we<sup>1)</sup> as well as Keehn *et al.*<sup>2)</sup> have synthesized [2.2](2,6)azulenophane (1), which showed some transannular  $\pi$ -electron interaction because of the heavy overlap of  $\pi$ -electrons of two dipolar azulene rings. In this paper we describe syntheses and physical properties of a [2.2]phane (3) and a dithia[3.3]phane (2), both with 1,3-bridged azulene rings.



**Synthesis** 1,3-Bis(mercaptomethyl)azulene, m.p. 70–71°C, obtained in 66% yield from azulene-1,3-bis-(methyltrimethylammonium) diiodide (4)<sup>3)</sup> by sodium hydrosulfide in boiling methanol, was coupled with 4 in dry methanol with NaOCH<sub>3</sub> (high dilution technique) to give in 54% yield 2,13-dithia[3.3]azulenophane (2), blue needles, m.p. 174°C (dec.);  $m/e$  372 ( $M^+$ , 100%), 185 (90), 155 (89);  $\nu^{KBr}$  1575, 1430, 743, 727  $cm^{-1}$ ;  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 271 (log  $\epsilon$  4.73), 299 (sh 4.49), 365 (3.86), 630 nm (2.70).

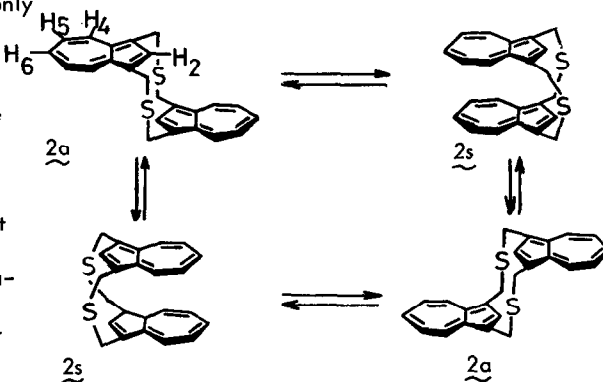
Photodesulfurization of 2 was achieved within 50 hr in a 3:1 mixture of trimethylphosphite and benzene to give in 16% yield [2.2](1,3)azulenophane (3), green plates, m.p. 202°C (dec.);  $m/e$  308 ( $M^+$ , 100%), 280 (88), 154 (92);  $\nu^{KBr}$  1570, 1430, 1301, 851, 741  $cm^{-1}$ ;  $\lambda_{max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 289 (log  $\epsilon$  4.75), 315 (sh 4.70), 366 (4.07), 380 (3.85), 415 (2.51), 646 nm (2.69).

**PMR spectrum of 3** PMR parameters observed are  $\delta$  (CDCl<sub>3</sub>) 2.56–3.72 (8H, m, AA'BB'), 4.39 (2H, s),

6.96 (4H, t,  $J=10$ ), 7.45 (2H, t,  $J=10$ ), 8.21 (4H, d,  $J=10$ ). Signals due to the bridge ethylene protons appear as AA'BB' pattern verifying a fixed conformation. The "stepped" (anti) conformation is suggested from a large upfield shift ( $\Delta\delta$ : 3.09 ppm), for inner aryl protons ( $H_2$ ) and downfield shift of outer aryl protons ( $\Delta\delta$ : 0.24 for  $H_4$ , 0.16 for  $H_5$  and 0.09 ppm for  $H_6$ ) compared with the corresponding signals of 1,3-dimethylazulene (5).

PMR spectrum of 2 The spectrum [ $\delta$  ( $CS_2$ ) 4.11 (8H, s), 6.60 (4H, t,  $J=10$ ), 6.96 (2H, s), 7.09 (2H, t,  $J=10$ ), 7.82 (4H, d,  $J=10$ )] at room temperature clearly shows a sharp singlet for bridge protons, suggesting the presence of a rapid dynamic process. That this dynamic process is the flipping of the azulene ring (2a and 2s) and not the conformational change in S-containing twelve-membered ring is clearly shown from the chemical shift of all aromatic protons: All signals have shifted upfield when compared with those of 5, but the shift value ( $\Delta\delta$ ) for  $H_2$  (0.52 ppm) is roughly twice as large as those of the other protons ( $H_4=0.15$ ,  $H_5=0.20$ ,  $H_6=0.27$  ppm). If 2 exists only

in the stepped conformation 2g, the outer protons ( $H_4$ - $H_6$ ) should shift downfield, judging from those in [2.2]metacyclophane (6)<sup>4,5</sup> and 3, while the upfield shift should be expected to the same extent for all aromatic protons in the "parallel" conformer 2s, as was observed in syn-[2.2](1,4)naphthalenophane<sup>6</sup>) and syn-[2.2](1,4)anthracenophane<sup>7</sup>).



Thus, neither 2a nor 2s alone can explain the observed upfield shifts. When PMR spectrum was measured at  $-120^\circ$ , the bridge protons change to two sets of broad AB pattern showing the slow down of the flipping<sup>8</sup>). Although kinetic parameters were not determined because of the limited solubility, this clearly shows that both 2a and 2s are the preferred conformers.

CMR spectrum of 3 Chemical shifts are shown in Table together with those of 5<sup>9</sup>). The chemical shift differences between the two are larger in five-membered ring than in seven-membered ring. The downfield shift of five-membered ring

Table <sup>13</sup>C Chemical Shifts (ppm) of 3 and 5

comps	positions (azulene numbering)					
	1,3	2	9,10	4,8	5,7	6
<u>3</u>	129.0	147.3	138.1	132.7	120.7	136.9
<u>5</u>	124.7	139.5	136.9	133.2	120.4	137.3

carbons on going from  $\underline{5}$  to  $\underline{3}$  are reasonably explained by steric compression effects<sup>10)</sup>, supporting the stepped conformation of  $\underline{3}$ .

X-ray analysis of  $\underline{3}$  The crystals of  $\underline{3}$  (recrystallized from the 1:1 mixture of benzene and cyclohexane) belong to monoclinic system with two molecules in the unit cell of dimensions,  $a=7.714(1)$ ,  $b=12.612(1)$ ,  $c=8.96(1)$  Å and  $\beta=109.93(1)^\circ$ . The space group is  $P2_1/a$ . The structure was solved by the direct method using 1503 unique reflections collected by CuK $\alpha$  radiation and refined by block-diagonal least squares

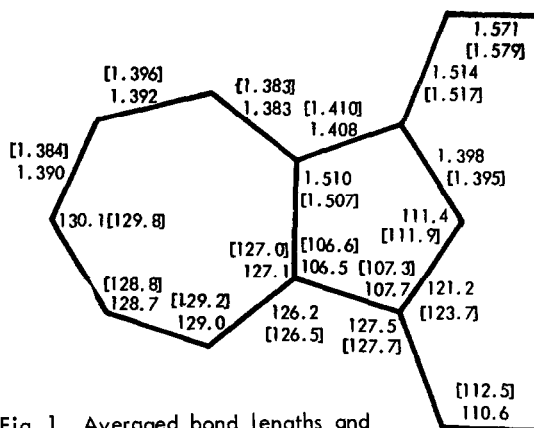


Fig. 1 Averaged bond lengths and angles of  $\underline{3}$  and  $\underline{7}$  in brackets

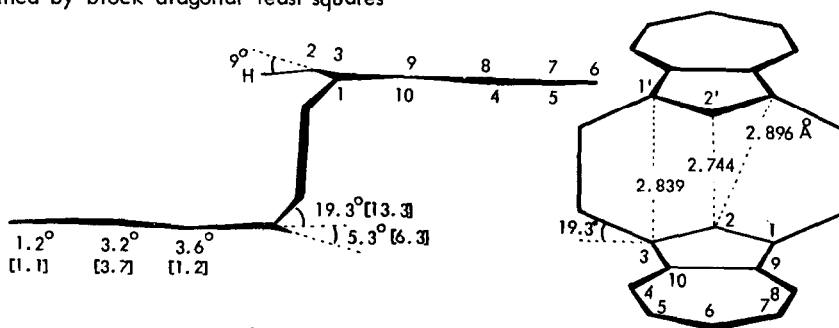


Fig. 2 Side views with interatomic distances and bending angles of azulene ring of  $\underline{3}$  and  $\underline{7}$  in brackets

calculations. The final R value is 7.1%. Since the molecule is situated on the crystallographic point of symmetry, one half of the molecule is independent. Averaged values of chemically equivalent bonds and angles are shown in Fig. 1 together with those of  $[\underline{Z}(1,3)\text{azuleno}[\underline{Z}]\text{paracyclophane}(\underline{7})$ <sup>11)</sup>. The bond lengths and angles are very similar between two compounds. Longer transannular bond (1.510 Å) in azulene ring is observed also in this case. The major distortion of the molecule is clearly seen in side views shown in Fig. 2 along with interplanar atomic distances and bending angles of aromatic rings. The shortest distance ( $C_2 \dots C_2$ , 2.744 Å) is slightly longer than that of  $\underline{6}^5$  (2.633 Å). The bending angle of exocyclic bond of azulene ring (19.3°) is, however, by far larger than the corresponding value of  $\underline{6}$  (13.3°) and  $\underline{7}$  (13.3°), showing a larger steric compression in this molecule, while bending angles of azulene ring are quite similar with those of  $\underline{7}$ . Only the inner aryl hydrogens bent considerably (9°) inward. Since there is no short

intermolecular contact which results in distortion of the molecule, all of these distortions should be due to intramolecular factors.

Electronic spectra The electronic spectrum of 3 is shown in Fig.3 together with that of 5 and Z. Although red shift of the longest wave length band ('Lb) is quite small ( $\sim 7$  nm), other bands ('La, 'Bb) exhibit a fairly large bathochromic shifts ( $\sim 15$  nm) when compared with those of 5. Moreover, two new bands appear at 315 nm and 400-450 nm. Since azulene rings bent almost to the same extent with that of Z and bathochromic shifts due to bending of aromatic ring<sup>12)</sup> is very small as was found in Z<sup>10)</sup>, the bathochromic shifts and the new bands observed are due mainly to transannular  $\pi$ -electron interaction between two facing azulene rings.

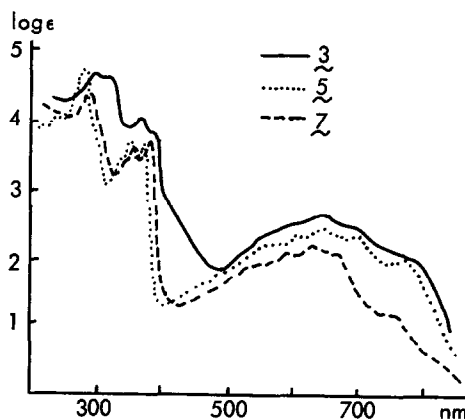


Fig.3 Electronic spectra of 3, 5 and Z

#### References and Footnotes

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