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AZULENOPHANE VIII. CONFORMATIONS OF DITHIA[3.3]AZULENOPHANES

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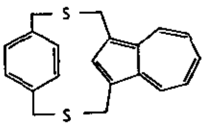
Dithia[3.3]metacyclophane and -metaparacyclophane are known to undergo dynamic processes which involve the flipping of two aromatic rings and conformational change of S-containing 12- or 13-membered ring. The former is also known to prefer syn conformation. In order to elucidate such conformational problems, and to understand the effect of the size of the bridging ring, and dipolar nature of azulene, dithia[3.3]azulenophanes 1 - 10, all of which were synthesized in our laboratory have been subjected to PMR spectroscopic investigations.



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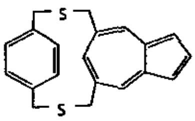

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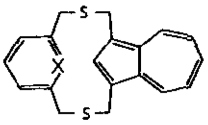
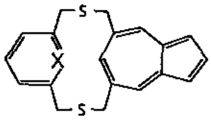


3 X=CH
5 X=N



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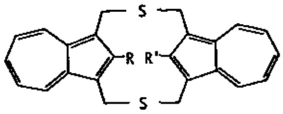
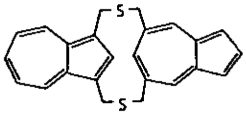


7 R=R'=H
8 R=Me, R'=H
9 R=R'=Me



10

All of these compounds display two aforementioned dynamic processes at room temperature as judged from singlet nature of the bridge methylene except 8 and 9 where methyl-substituted azulenes stop flipping. In the latter cases neighboring methylenes exhibit AB pattern.

9 exists as two discrete syn and anti conformers (9s and 9a). In the syn conformer 9s all azulenic protons show up-field shifts and methyl group down-field shifts when their chemical shifts are compared with those of 1,2,3-trimethylazulene. Reverse is true for 9a.

The activation energies ($\Delta G^{\ddagger}$) for the ring flipping in azulenocyclophanes 1, 2, were calculated to be 7.0 kcal/mol and <7 kcal/mol, respectively. Inner protons show rather large up-field shift from which their time-averaged positions are suggested. Metacyclophanes, 3 and 4, and pyridinophanes, 5 and 6, prefer syn conformation, as is judged from the shift values of the aromatic protons and low temperature study. $\Delta G^{\ddagger}$ for 3 and 4 were calculated to be ~10.5 kcal/mol and ~10 kcal/mol, respectively.

Syn conformation is preferred for azulenophanes 7 and 10, at -120°C, 7 exists as a 7:3 mixture of syn and anti conformers. Therefore the former is ca. 0.3 kcal/mol more stable than the latter. $\Delta G^{\ddagger}$ for 7 is estimated to be ~9 kcal/mol. On the other hand 10 exists entirely in syn form at -70°C, indicating the potential energy difference of two forms to be at least 1.5 kcal/mol. Calculated $\Delta G^{\ddagger}$ for the ring flipping is 12 kcal/mol.

The preferred syn conformation in all possible cases is attributed to be the non-bonded repulsion in the bridge of anti form. The difference in $\Delta G^{\ddagger}$ between 7, 3, 4, and 10 is probably originated from the intramolecular transannular interaction between two dipolar azulene moieties in the syn forms. The interaction stabilizes syn form of 10 and destabilizes that of 7, while in 3 and 4 no such interaction is present.