Chemistry of Benzologs of 4-Thiopyrone

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The six compounds studied contained one, two or three benzene rings fused to each other or to the thiopyrone ring. Of the six, three have not been previously reported. The M.O.-L.C.A.O. method with the Hückel approximation has been used to calculate the π-electronic energy levels, bond orders, electron densities, localization energies and super-delocalizabilities. The calculations were made both assuming and neglecting participation of the d-orbital of the sulfur. Reasonably good straight line relationships were found between the calculated and experimental $N \rightarrow V_1$ transition energies (spectra determined in cyclohexane).

The calculated bond orders and charge densities indicated that there is a considerable degree of delocalization in the thiopyrone ring, and strong conjugation between sulfur and oxygen, with a greater separation of charge than in the oxygen analogs. The carbonyl vibrations are found at unusually low frequencies (1615-1640 cm^{-1}), again showing strong conjugation. The carbonyl frequency of 5,6-benzothiochromone is exceptionally low at 1615 cm^{-1}, suggesting the possibility of C-H-O hydrogen bonding with the 6' position; the proton in this position has a distinctive and very high chemical shift in the n.m.r. spectrum, at 10.1 p.p.m (TMS = 0).

The low bond order of the C=O bond suggests that the oxygen could be considered as an integral part of the π-electronic system. It therefore seems permissible to regard the polarographic half--wave potential in aprotic conditions as a measure of the energy required to put one electron in the lowest vacant π orbital. Accordingly, measured half wave potentials (dimethylformamide) were plotted against calculated LV orbital energies, and satisfactory correlation was found.

A comparison of the pyrolysis of dibenzothiophene and thioxanthen-9-one at 600°and 800° showed the former compound to be much more stable thermally; whereas the sulfur in the thiophene derivative was mostly retained in the carbonaceous char, in the pyrolysis of the thioxanthenone it was mostly released as sulfur dioxide.