THE HOMOTHIOPYRYLIUM IONS

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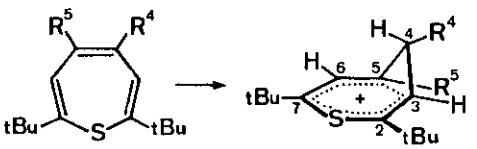
In contrast to the vast amount of literature concerning the preparation and characterization of the carbocyclic homoaromatic ions, no direct observation of the corresponding heterohomoaromatic ions has been reported so far. In view of the precedent that on protonation cyclooctatetraene easily converted into the homotropylium ion, the thiepins 1a, 1b, and 1c are expected to be promissing candidates for the formation of the homothiopyrylium ions such as 2a, 2b, and 2c, respectively.

Treatment of a CD_2Cl_2 solution of 2,7-di-t-butylthiepin (1a) with a solution of FSO_3H in SO_2 at -78 °C gave the 2,7-di-t-butyl-3,5-homothiopyrylium ion (2a) (as an orange solution). The ^1H NMR spectrum of the solution indicates (i) charge delocarization over the six-membered ring framework, (ii) fairly large chemical shift difference ($\Delta\delta$ = 2.5 ppm) between two methylene protons (H_{4o} and H_{4i}), (iii) gemical coupling constant of 11.6 Hz for these protons. These findings are consistent with the homothiopyrylium ion structure 2a. The same ion was also formed when 1a was dissolved in conc. H_2SO_4. The ^1H NMR spectrum of this solution at room temperature shows essentially the same signals except methylene protons which appear at δ 2.66 as a broad singlet. The ^1H NMR spectrum of 2a is temperature dependent due to the ring flipping. The $\Delta G^{\ddagger}$ value for the ring flipping is found to be 13.0 kcal/mol.



1 2

a, $R^4=R^5=H$
b, $R^4=CH_3$, $R^5=H$
c, $R^4=R^5=CH_3$

On protonation, 1b and 1c also converted to the corresponding homothiopyrylium ions, 2b and 2c, respectively. Protonation of 1-benzothiepin will also be discussed.