CHEMISTRY LETTERS, pp. 1759-1762, 1986.

DIMINUTION OF AROMATICITY IN HOMOTROPYLIUM IONS BY DONOR SUBSTITUENTS AND THE SITE-DEPENDENCE THEREOF

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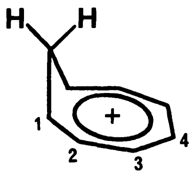
The aromaticity of homotropylium ions is shown to diminish in the order: parent > 4-OH > 2-OH > 1-OH > 3-OH. Diatropicity and thermodynamic stability both appear to follow this same order.

The dramatic difference in ^{1}H NMR chemical shift between the endo and the exo methylene hydrogens in homotropylium ion (**1a**, $\Delta\delta$ = 5.86 ppm)[1] and its derivatives has generally been regarded as evidence for a large diamagnetic ring current in such ions.[2-7] In consonance with this view, it has been observed that the introduction of a strong donor substituent, such as an OH group, onto the homotropylium ion nucleus always reduces the value of $\Delta\delta$ (e.g., **1b**,[8] **1c**,[9,10] and **1e**[11]).



a = parent ($\Delta\delta$ = 5.86)
b = 1-OH ($\Delta\delta$ = 3.08)
c = 2-OH ($\Delta\delta$ = 3.28)
d = 3-OH (unknown)
e = 4-OH ($\Delta\delta$ = 4.6)

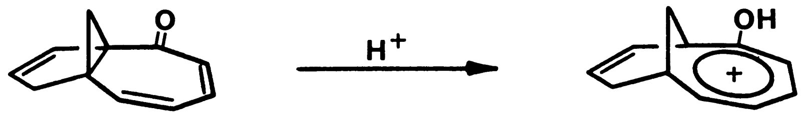
Stabilization of the positive charge by a substituent lessens the driving force for electron delocalization around the cycle and thereby diminishes the ring current, which reduces the value of $\Delta\delta$. This trend is based on spectroscopic studies of more than 15 different OH-substituted homotropylium ions;[10] however, data on 3-hydroxyhomotropylium ions have been particularly scarce until now.[12]

In this letter we show not only that attachment of an OH group to the 3-position of a homotropylium ion reduces the ring current but that it does so by even more than the amounts reported for OH-substitution at the 1-, 2-, or 4-position. We further note the existence of a correlation between the observed values of $\Delta\delta$ (ring current) and the apparent order of thermodynamic stability ("aromaticity") for OH-substituted homotropylium ions.

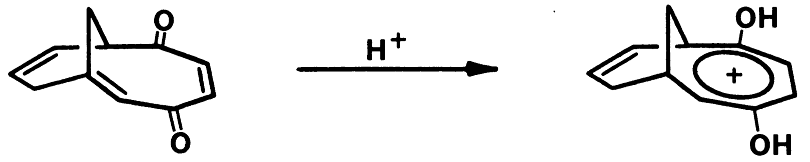
Several new OH-substituted homotropylium ions have been generated13) and examined by ^1H NMR spectroscopy in our laboratory, starting from precursors that we have reported elsewhere.12,14,15) Ions **3**, **5**, and **7** belong to the previously unknown class of 3-hydroxyhomotropylium ions, and all three are characterized by unusually small $\Delta\delta$ values. The effect of the 3-hydroxy group in these ions can be segregated from the influence of other structural features by using ions **2**, **4**, and **6** as reference points. Thus, a comparison between the $\Delta\delta$ values of ions **2** and **3** reveals that a 3-hydroxy substituent can significantly diminish the ring current even in a homotropylium ion which has already been strongly perturbed by one OH group. Ions **4** and **5**, on the other hand, represent the first pair of homotropylium ions in which the effects of 4-hydroxy substitution and 3-hydroxy substitution can be compared directly; the greater influence of an OH group in the 3-position is clearly evident. Finally, the 3-hydroxy group in **7** causes a full 50% reduction in the $\Delta\delta$ of **6**, which is already reduced by 13% relative to that of the parent homotropylium ion, **1a**.

From the foregoing NMR data, it can be seen that the effect of OH-substitution on the ring current of homotropylium ions is actually greater at the 3-position than at any other site. Thus, the ring currents of hydroxy-substituted homotropylium ions decrease in the order: 4-OH > 2-OH > 1-OH > 3-OH.

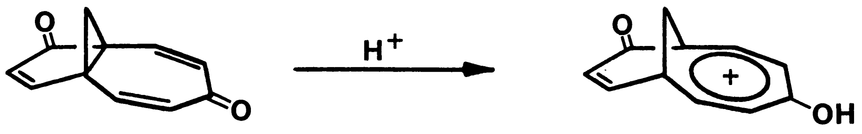
Though it has not been widely recognized, the thermodynamic stability of hydroxy-substituted homotropylium ions appears to follow this same order. Childs and coworkers have shown16) that 8,8-dimethyl-1-hydroxy homotropylium ion rearranges to the 2-hydroxy isomer even at -30 °C, presumably by a circumambulatory rearrangement in the bicyclo[5.1.0]octadienyl tautomer. At -16 °C, the 2-hydroxy isomer rearranges further to the 4-hydroxy isomer, presumably *via* the 3-hydroxy isomer, which never accumulates.16) Thus, we conclude that there is a direct correlation between the thermodynamic and the magnetic criteria for aromaticity in hydroxy-substituted homotropylium ions.



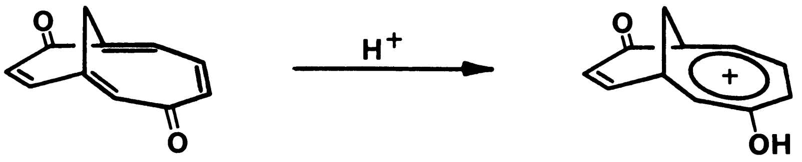
2 ($\Delta\delta$ = 2.89)



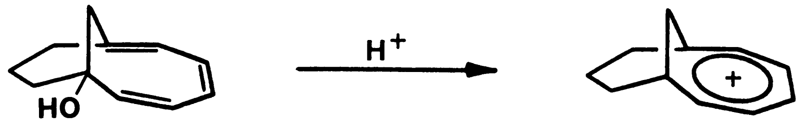
3 ($\Delta\delta$ = 2.52)



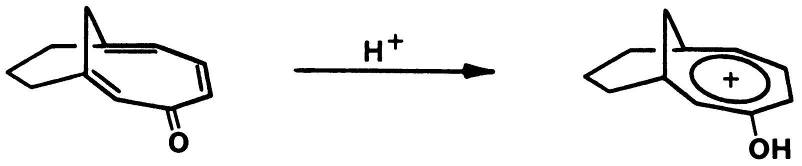
4 ($\Delta\delta$ = 2.83)



5 ($\Delta\delta$ = 2.41)



6 ($\Delta\delta$ = 5.09)



7 ($\Delta\delta$ = 2.53)

Financial support for this work from the U.S. National Science Foundation and National Institutes of Health is gratefully acknowledged.

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(Received July 22, 1986)