The tropolones make up a very interesting class of nonbenzenoid aromatic compound that was discovered first in several quite different kinds of natural products. As one example, the substance called \(\beta\)-thujaplicin or hinokitiol has been isolated from the oil of the Formosan cedar and is 4-isopropyltropolone:

![4-isopropyltropolone](image)

Tropolone itself can be prepared in a number of ways, the most convenient of which involves oxidation of 1,3,5-cycloheptatriene with alkaline potassium permanganate. The yield is low but the product is isolated readily as the cupric salt:

![Tropolone synthesis](image)

The cycloheptatriene for this synthesis can be obtained best by thermal rearrangement of the Diels-Alder addition product of cyclopentadiene and ethyne:

![Diels-Alder addition product](image)

Tropolone is an acid with an ionization constant of \(10^{-7}\), which is intermediate between the \(K_a\) of ethanoic acid and the \(K_a\) of benzenol. Like most arenols, tropolones form colored complexes with ferric chloride solution. Tropolone has many properties that attest to its aromatic character - it resists hydrogenation, undergoes diazo coupling, and can be nitrated, sulfonated, and substituted with halogens. The aromaticity of tropolone can be attributed to resonance involving the two nonequivalent VB structures \(6a\) and \(6b\), and to several dipolar structures, such as \(6c\) and \(6d\), in which the ring has the stable tropylium cation structure with six \(\pi\) electrons (Section 21-9B):

![Resonance structures](image)

The tropylium cation is prepared easily by transfer of a hydride ion from cycloheptatriene to triphenylmethyl cation in sulfur dioxide solution. This reaction is related to the hydride ion transfer, \(\text{C_6H_5CH}_3^+ + \text{RH} \rightarrow \)
Seven equivalent VB structures can be written for the tropylium cation so only one seventh of the positive charge is expected to be on each carbon. Because the cation has six \( \pi \) electrons, it is expected from Huckel’s \( \left( 4n + 2 \right) \) \( \pi \)-electron rule to be unusually stable for a carbocation.

The infrared and Raman spectra of tropylium bromide in hydrobromic acid solution have no common bands, which means that the cation exists in a highly symmetrical form in this solution (see Section 9-8). At higher pH, reversible formation of the hydroxy compound occurs:

\[
\text{[C}_7\text{H}_7^+ + \text{OH}^- \rightleftharpoons \text{C}_7\text{H}_7\text{OH}}]
\]

The equilibrium constant for this reaction is such that the cation is half converted to the hydroxy compound at about pH 5.

Colchicine is an important naturally occurring tropolone derivative. It is isolated from the autumn crocus and is used in medicine for the treatment of gout. It also has an effect on cell division and is used in plant genetic studies to cause doubling of chromosomes. The structure has been confirmed by total synthesis.

Contributors