

VII-D Unusual Reactivities of N-Heterocycles

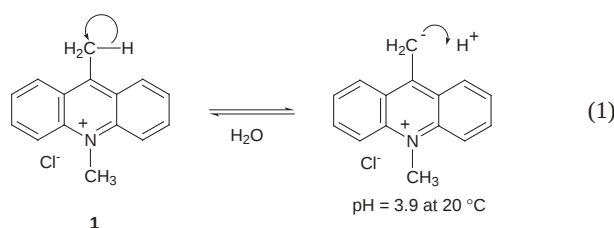
Among aromatic nuclei, acridines and their derivatives are still attracting considerable attention because of the many functions which they possess, including biomimetic redox reactivities, chemiluminescence, and the interaction with DNA as an intercalator. In particular the 9 position, the para position from acridine nitrogen, in acridinium exhibits strong electrophilicity and reacts with alcohols giving rise to 9-alkoxyacridanes. 9-methyl substituted acridinium exhibited a slightly different reactivity with basic alcohol, affording the corresponding 9-alkoxyacridanes followed by an olefinic species, 9-methyleneacridane, through the 9-methyl proton abstraction by an alkoxide. Therefore, the 9 position in acridinium appears to have different electric and steric conditions as compared to the other positions, giving rise to expectations of more unique reactivity. Here we report on the unusual reactivities of the acridinium skeleton as a N-Heterocycle.

VII-D-1 An Unusually Acidic Methyl Group Directly Bound to Acridinium Cation

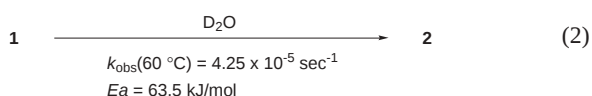
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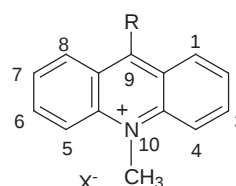
9,10-dimethylacridinium chloride (**1**; X = Cl) exhibited strong acidity of pH 3.90 (3.4×10^{-3} M, 20 °C) in an aqueous solution. H-D exchange reaction of **1** in D₂O indicated that protons in the 9-methyl group dissociated to generated H⁺ ions (equation 1). This is an



unique example of a methyl proton functioning as an acid. The conversion of **1** into **2** followed first-order kinetics with respect to the concentration of **1** over the temperature range studied (equation 2). The acidity



derives from the wider π face in acridinium capable of delocalizing the newly formed negative charge upon proton dissociation. PM3 calculations provided stabilization factors ($\delta\Delta H_f^\circ$) between proton dissociated and undissociated forms of several N-heterocycles and also confirmed the acidity observed in acridinium.



- 1:** R=CH₃, X=Cl, I, CH₃SO₄
2: R=CD₃, X=Cl, I, CH₃SO₄

Figure 1. Chemical Structures of **1** and **2**.

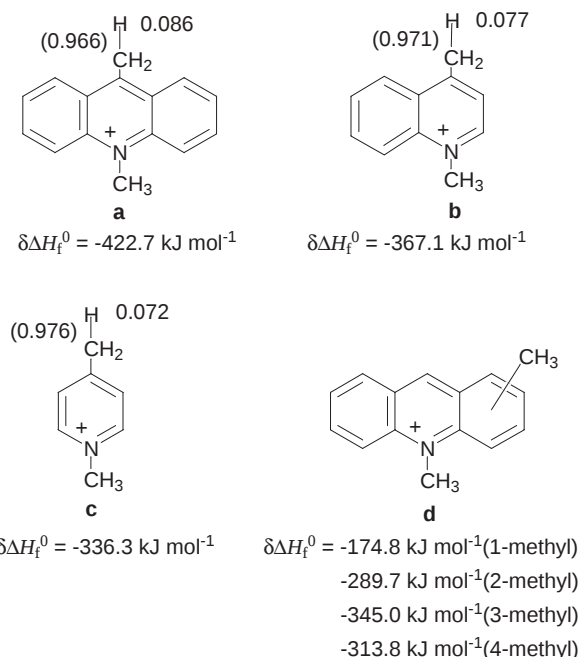


Figure 2. Model Structures for the PM3 calculation. The numbers in the structures refer to the partial charges of the dissociating proton. The numbers in parentheses refer to the bond orders between the proton and an atom bound to the proton. The difference in heat of formation ($\delta\Delta H_f^\circ$) was calculated from ΔH_f° (undissociated form) + ΔH_f° (H₂O) – ΔH_f° (dissociated form) – ΔH_f° (H₃O⁺).