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 pare 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

![Figure 1. Chemical Structures of 1 and 2.](image)

![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 (δΔH°) was calculated from ΔH° (undissociated form) + ΔH° (H₂O) - ΔH° (dissociated form) - ΔH° (H₃O⁺).](image)

δΔH° = -422.7 kJ mol⁻¹
δΔH° = -367.1 kJ mol⁻¹

δΔH° = -336.3 kJ mol⁻¹
δΔH° = -174.8 kJ mol⁻¹ (1-methyl)
δΔH° = -289.7 kJ mol⁻¹ (2-methyl)
δΔH° = -345.0 kJ mol⁻¹ (3-methyl)
δΔH° = -313.8 kJ mol⁻¹ (4-methyl)