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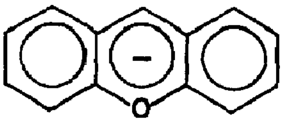
GENERATION AND DIRECT OBSERVATION OF THE THIOXANTHENYL AND N-METHYL ACRIDINYL ANIONS; A FAMILY OF STABLE, PARATROPIC, "4N" π-EXCESSIVES

A. G. Anastassiou, H. S. Kasmai[1] and M. R. Saadein

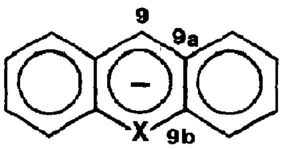
Department of Chemistry
Syracuse University
Syracuse, New York 13210

The title, thermally stable, heterocarbanions (2a, 2b) were generated upon respective exposure of conjugate acids 4(a,b) to a KNH_2/liq. NH_3 system and were shown (NMR) to possess (2a more than 2b) distinct elements of paratropicity.

Direct spectroscopic scrutiny of potentially antiaromatic, predictably unstable, 4n-electron "Huckel" π systems has long been deemed to be a fundamentally significant aspect of research work directed at probing the phenomenon of "aromaticity". Having recently been greatly encouraged by the successful generation and NMR examination of the decidedly paratropic, yet thermally stable, xanthenyl anion 1[2] we resolved to extend our work in the area and naturally did so first by concentrating on two skeletally related basic heteroatomic variants of 1, specifically 2a and 2b.



1



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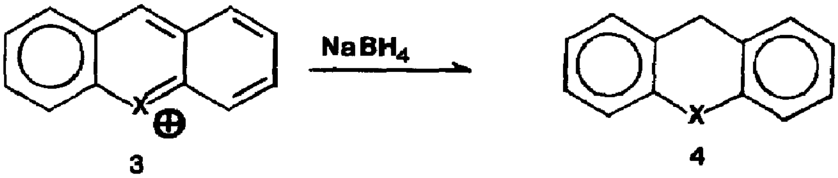
a; X=NMe
b; X=S



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The two conjugate-acid progenitors 4(a,b)[3] of the desired heterocarbanions 2(a,b) were prepared cleanly upon treatment of the respective "onium" salts 3(a,b) with ethanolic sodium borohydride.[3] Exposure of 4a and 4b to KNH_2 in liquid ammonia led, respectively, to 2a[4] [^{1}H-NMR (Fig. 1A); ^{13}C-NMR, 20 MHz, NH_3~30°C, H-coupled (δ_{THF},[5] - 34.91 ppm (q, Me), 7.36 (d,C^9), 40.05(d), 41.20(d), 42.39(d), 56.13(d), 75.02(s), 78.78(s)] and 2b [^{1}H-NMR (Fig. 1B); ^{13}C-NMR, 20 MHz, NH_3, ~30°C, H-coupled (δ_{THF},[5] 14.77 ppm (d,C^9), 44.71(d), 46.60(d), 46.60(s,C^{9b}), 57.64(d), 60.12(d), 81.30(s,C^{9a})].

The recorded NMR data contain a number of informative features the most immediately obvious being, of course, the rather major shielding experienced by the system's formally "benzenoid" protons.[5] In fact, recalling that a closely related display of shifts by the oxygen analog 1 was recently shown to be due primarily to the effect of molecular paratropicity,[2,7] and noting that the stated shifts in the case of azacarbanion 2a (Figure 1A) are actually <u>greater</u> (by ca. 0.2 ppm) than those of 1, we deduce that the π frame of 2a may also be securely classified as paratropic. Further strong indication of the presence of a paramagnetic ring current in 2a derives from the rather striking upfield shift (ca. 1.0 ppm) experienced by the N-methyl function on passing from 4a(τ 6.60) to 2a(τ 7.65).

Direct NMR comparison between heterocarbanions 1[2] and 2a on the one hand and their sulfur relative 2b reveals some fundamental differences attributable chiefly to the second-row nature of sulfur. In brief what one finds is that whereas the "benzenoid" proton shifts clearly require 2b to be less paratropic than either 1[2] or 2a, the key carbanionic shifts, respectively observed at $\tau(H^9)$ 6.92, 6.80, 6.08 and $\delta_{THF}(C^9)$ 0.33, 7.36, 14.77 ppm for 1[2], 2a and 2b, decidedly reveal the carbanionic center of 2b to be the <u>least</u> localized of the three! This obvious operational inconsistency whereby heteroatom effectiveness within the system increases in the order $O < NMe <$ with regards to the extent of carbanionic delocalization and $S < O \sim NMe$ with respect to the development of paratropicity is, we believe, most rationally attributable to the sulfur atom's ability as a second-row element to stabilize an adjacent negative charge.

We conclude by calling attention to the fact that the degree of NMR-measured paratropicity of the two "normal" first-row heterocarbanions, <u>i.e.,</u> 2a > 1, exhibits the expected inverse relationship to the magnitude of the HMO energy gap between HFMO(ψ_8) and LVMO(ψ_9).[8]

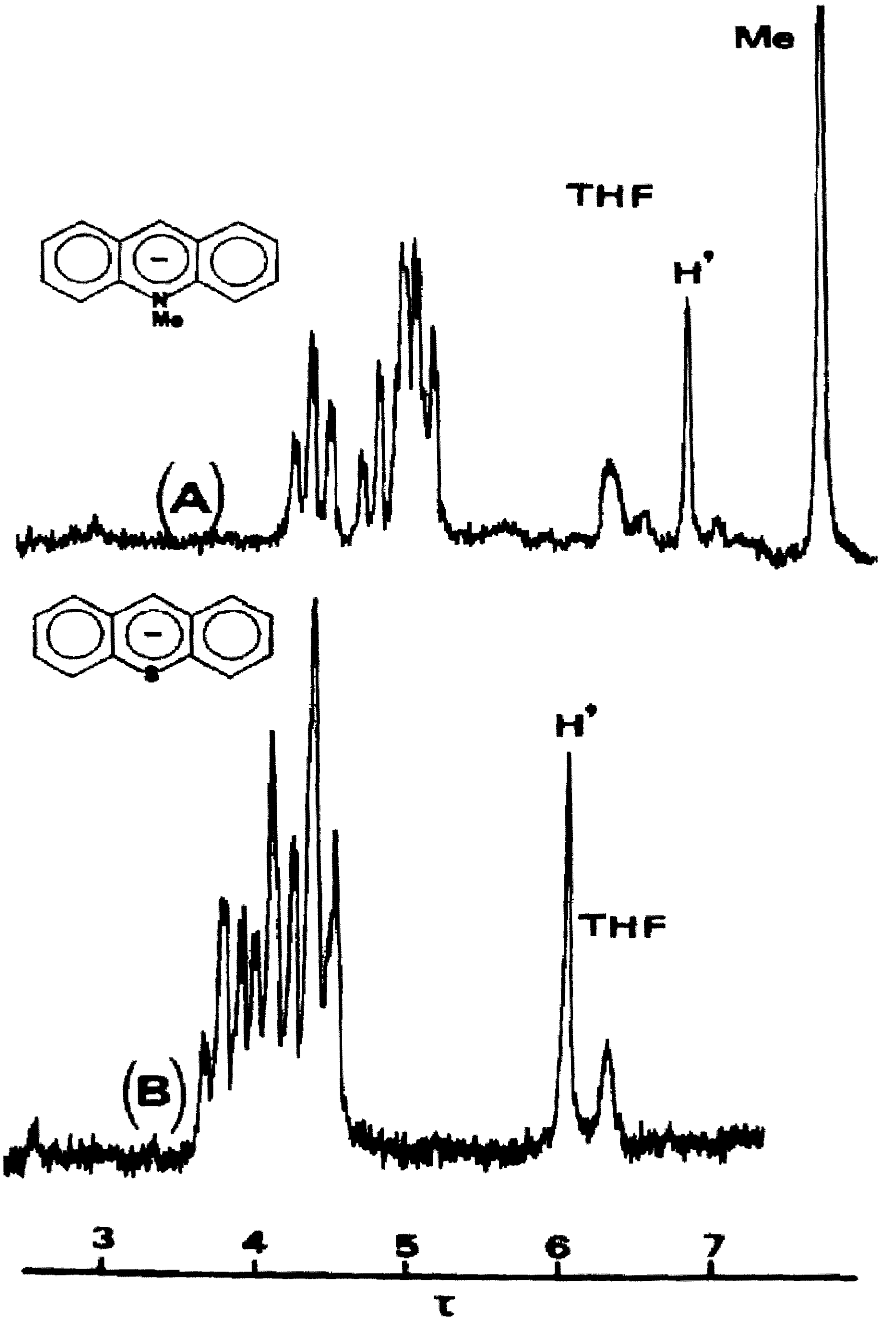

Figure 1 ^{1}H-NMR spectrum of (A) N-methyl acridinyl anion (2a) and (B) thioxanthenyl anion (2b) recorded at 60 MHz in liquid ammonia (THF as internal standard) and ca. 34°C.

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References and Notes

(1) On sabbatical leave from the Department of Chemistry, Shiraz University, Shiraz, Iran.

(2) A. G. Anastassiou and H. S. Kasmai, *Angew. Chem.*, **92**, 53 (1980).

(3) We thank Mr. Paul Ruggieri for the preparation of these substances.

(4) This species was first generated in our laboratories by Ms. Susan Stanton.

(5) Measured downfield shift from the central signal of the low-field multiplet of THF-d_8 (δ_{TMS} 67.9 ppm).

(6) In conjugate acids **4a** and **4b** the "benzenoid" protons give rise to narrow multiplets centered at τ 2.9 and 2.8 respectively.

(7) The classification of **2a** as paratropic follows primarily from direct NMR comparison with potassium diphenylmethide whose major absorption manifold (8H) in the ^{1}H-NMR spectrum appears at a substantially lower field (ca. 1.8 ppm) than its 6H counterpart in the spectrum of **2a**. Further evidence that the indicated shift is due predominantly to the presence of paratropicity in **2a** rather than a shielding "charge effect" derives from ^{13}C-NMR information which requires that the key benzylic charge at C^9 be more extensively delocalized in the model diphenylmethide (δ_{TMS} = 81.33 ppm) than in **2a** (δ_{TMS} = 75.26 ppm)

(8) Based on a simple first order HMO perturbation treatment with chosen parameters: $h_{C^-} = -1.0$, $h_O = +2.0$, $h_{NMe} = +1.0$, $\Delta\varepsilon(9,8)$ is estimated at 0.59β for **2a** and 0.78β for **1**.

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