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THE POTENTIALLY ANTIAROMATIC (4N-π) α-HETERONAPHTHALENYL ANIONS

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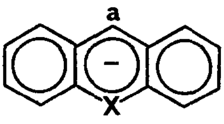
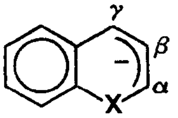
Representative members of the title family of compounds were generated in liquid ammonia, and the "thia" analog 2c was sufficiently stable as to be directly examined by NMR.

In recent reports we described the generation and NMR-based classification of the potentially antiaromatic (16π) hetero-π-excessive carbanionic systems shown in 1.[1,2] In order to further probe into the nature of paratropic delocalization we have now examined the skeletally less restricted monobenzo analogs of 1, namely 2.



1

a ; X = NMe
b ; X = O
c ; X = S



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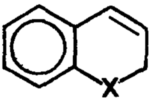

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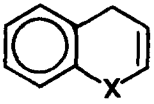

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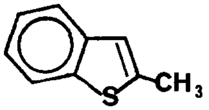


5

Although all three heterocarbanions 2 (a,b,c) appear to have been generated from progenitors 3[3] and/or 4[4] on exposure to KNH_2 in liq. NH_3 at ca. -35°C, only the thia analog 2c[5] was sufficiently stable as to be amenable to direct NMR observation, its ^{1}H spectrum consistently displaying a 5H multiplet ($H^{benzenoid} + H^{\beta}$) extending from δ5.6 to δ6.4 and two 1H doublets of doublets centered at δ3.88 (H^{γ}, J = 7.0, 1.5 Hz) and δ2.0 (H^{α}, J = 6.0, 1.5 Hz).[6] Nonetheless, anion 2c is not a thermally stable substance readily rearranging to 5, mp 52-53°C (lit.[7] 51°-52°C) upon warming to 0°C.[8]

Concluding, we note that while none of the three heteroatomic carbanions described in this report is thermally stable, 2c is substantially more so than its first row relatives 2a and 2b the thermal stability sequence being in the order 2c > 2a ~ 2b[9]. Further, direct comparison of this sequence to our earlier classification[2] of the dibenzo analog 1c[2] as significantly less paratropic than either of its two first-row relatives 1a,[2] 1b[1] offers convincing demonstration of the often assumed but rarely proven existence of a direct correlation between ring paramagnetism and "anti-aromatic" destabilization.

Acknowledgement: We are grateful to the National Science Foundation for support of this work.

References and Notes

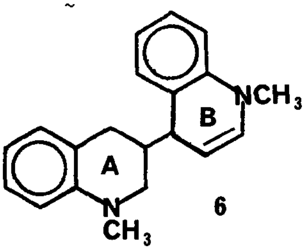
(1) A. G. Anastassiou and H. S. Kasmai, *Angew Chem.*, 92, 53 (1980); *Angew Chem. Int. Ed. Engl.*, 19, 43 (1980).

(2) A. G. Anastassiou and H. S. Kasmai, and M. R. Saadein, *Tetrahedron Lett.*, 3743 (1980).

(3) a. Preparation of 3a: E. A. Brande, J. Hannah and R. P. Linstead, *J. Chem. Soc.*, 3249 (1960); b. Preparation of 3b: W. E. Parham and L. D. Huestis, *J. Am. Chem. Soc.*, 84, 813 (1962); c. Preparation of 3c: W. E. Parham and R. Konocos, *J. Am. Chem. Soc.*, 84, 4034 (1961).

(4) a. Preparation of 4a: A. J. Birch and P. G. Lehman, *J. Chem. Soc.* (Perkin I), 2754 (1973); b. Preparation of 4b: ref. [3c]; c. Preparation of 4c: ref. [3c].

(5) The response of solutions of 3 and/or 4 in KNH_2/NH_3 to methanolic quench (-35°C) is strictly dependent on the nature of the heteroatom for while 2c yields a 1:1 mixture of 3c and 4c, 3b (4b) produces intractable tars and 3a (4a) affords what is believed to be (^{1}H-NMR, ^{13}C-NMR, MS) the dimeric product shown in 6.

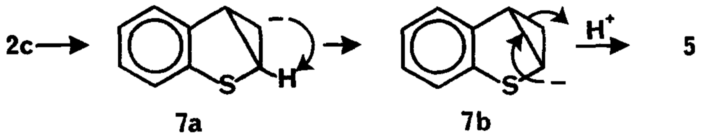


6

(6) Confirmation of the specific NMR assignments follows from related work and γ-deuterio 3c whose anion, γ-deuterio 2c, displays an ^{1}H-NMR spectrum initially lacking the low field H signal at δ3.88.

(7) M. Pailer and E. Romberger, *Monatsh. Chem.*, 91 1070 (1960).

(8) a. The structure of 5 securely follows from its fully consistent ^{1}H-NMR, ^{13}C-NMR and mass spectrometric characteristics; b. Mechanistically, the 2c to 5 transformation may be viewed to occur as follows:



(9) It was pointed out by a reviewer that this comparison of relative stabilities may not be entirely valid insofar as it is not clear whether anions 2a and 2b degenerate intra- or intermolecularly although the formation of dimeric product 6 does, of course, establish that azaanion is consumed, at least in part, intermolecularly. While this criticism is certainly not unreasonable it is well to stress that our conclusion about relative stabilities is based on the *overall* ability of the three anions 2(a,b,c) to survive within a common environment and is *thus* valid irrespective of whether molecular degeneration obtains intramolecularly (as in the case of 2c) or intermolecularly (as is chiefly the case with 2a).

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