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A ^{13}C-NMR STUDY OF BICYCLOCONJUGATION AMONG BENZANNULATED 9-HETEROBICYCLO[4.2.1]NONA-2,4,7-TRIENES

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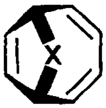
The question of heterobicycloconjugation among certain newly prepared symmetrically benzannulated 9-heterobicyclo[4.2.1]nona-2.4.7-trienes (**3**) was examined by ^{13}C-NMR with results entirely supportive of the simple theoretical operatives developed earlier.

The phenomenon of bicycloconjugation as it relates to conventional cyclic delocalization and/or the development of "aromatic" or "antiaromatic" character has received considerable attention in recent years and it may safely be stated that three-unit p-π interaction (bicycloconjugation) is most securely associated with ionic species, i.e., systems consisting of a relatively high energy and thus readily perturbable unit. Our own interest in extending the basic concept into the area of π-excessive heterobicyclic frames, e.g. **1**, and the development of heterobicycloconjugation has led us to propose a three-step interaction process whose crucial first step entails isosymmetric interaction between the heteroatomic lone pair and the system's "4n+2" unit (ethylene in **1**, naphthalene in **2** and benzene in **3**) and whose activation may be triggered only if the former (lone pair) is positioned at a higher energy than the latter. Within the frame of this simple operational scheme we were able to rationally explain the existence (by PES and ^{13}C-NMR)[2,3] of heterobicycloconjugation in parent azabicycle **1a** as well as its conspicuous absence (by ^{13}C-NMR)[4] in the naphtho-fused relative **2a**.

In an effort to further assess the viability of this simple predictive process within the frame of our commonly utilized experimental procedure, i.e., ^{13}C-NMR[3,4], we resolved to examine yet another derivative of **1** namely the benzannulated variant **3** whose "aza" member **3a** is predicted to possess not only the correct ordering of key energy levels[5] but also one associated with an energy difference (0.23eV)[5] which is significantly smaller than its counterpart in **1a** (0.66eV)[5], thus enhancing the potential of **3a** to sustain bicycloconjugation over and above that of **1a**.



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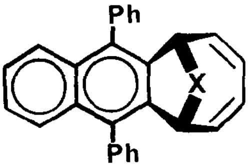

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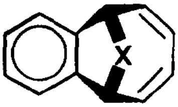

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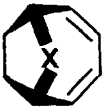

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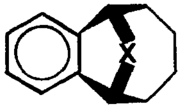

5

6

a ; X = NH
b ; NCN
c ; O
d ; S
e ; CH_2

Synthetic entry[6] into the desired "aza" members of the series **1***(a,b),* **5***(a,b) was gained* through **1b**[7] while the "thia" counterparts **3d**, **5d** were prepared via sulfone **3**($X{=}SO_2$)[8]. The method of analysis employed throughout the present study utilizes changes in "bridgehead" *CH* coupling constants on passing from suitably selected models to **3** through basic steps which are entirely analogous to those described earlier for parent **1**[3] and naphannulated variant **4**[4].

Table. ^{13}CH "bridgehead" coupling constants (Hz) of **3** and **5** as well as pertinent ΔJ terms [a].

X	**3**	**5**	$\Sigma[\Delta(6\rightarrow4),\Delta(6\rightarrow5)]$	$\Delta(6\rightarrow3)$	$E_J(3)$[b]
NH	160	146	11	22	11
NCN	152	148	6	7	1
S	147	143	5	7	2

a. The values of J_{CH} pertaining to models **4** and **6** are those listed in an earlier publication[3].

b. The term $E_J(3)$ stands for the J_{CH} "exaltation" of **3** and is given by the difference between $\Delta(6\rightarrow3)$ and $\Sigma[\Delta(6\rightarrow4),\ \Delta(6\rightarrow5)]$.

Brief examination of the tabulated information in terms of key quantity E_J reveals the parent "aza" member of the family, **3a**, to be well endowed (11Hz) and measuring nearly twice as much as its debenzo relative **1a** (E_J=6Hz)[3]! Gratifyingly, this result is entirely in keeping, at least qualitatively, with the prediction arrived at from energy considerations of key filled levels within the frame of our proposed interaction scheme (vide supra). In further confirmation of the viability of this scheme we find cyanamide **3b** (a good "energy" model for the as yet unavailable ether **3c**) whose unperturbed lone pair [n_s(**4b**)=9.40eV][5c] is lower in energy than the unperturbed frontier MO of the frame's benzenoid moiety [π_3(**3e**)=8.59eV][5b] to possess virtually no J_{CH} "exaltation", E_J(**3b**)≈1Hz, and thus not to be bicycloconjugated. Interestingly, the "thia" analog **3d** is equally lacking in this connection (E_J≈2Hz) although here the absence of bicycloconjugation cannot be attributed to improper energetics (ΔE=0.33eV)[5] but may rather be viewed as being due to the effect of sulfur-induced "back-donation"[3,4].

Summarizing, we note that the combined information extracted from this and earlier work[3,4] on the general 9-heterobicyclo[4.2.1]triene frame allows one to derive the following theory-supported sequence with regards to the "aza" members of the family and their ability to sustain heterobicycloconjugation[9].

3a(0.23eV;11Hz) > 1a(0.66eV;6Hz) >> 2a(-0.34eV;1Hz)

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References and Notes

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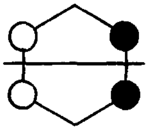
(2) H. Schmidt, A. Schweig, A. G. Anastassiou and H. Yamamoto, Chem. Commun., 218 (1974).

(3) A. G. Anastassiou and E. Reichmanis, J. Am. Chem. Soc., **98**, 8267 (1976).

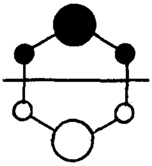
(4) A. G. Anastassiou, H. S. Kasmai and R. Badri, Angew. Chem., **92**, 657 (1980)

(5) π_3(benzene)[a](**3e**)=8.59eV[b], n_s(**4a**)=8.36eV[2], π_1(ethylene)(**1e**)=9.02eV[2], n_s(**4d**)=8.26eV[d]

a. Fully as anticipated from simple perturbation theory, π_3 of benzene in **3** is given by the plane-symmetric representation shown in (i) and not the plane-antisymmetric counterpart (ii).



(i)



(ii)

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d. C. Miller, A. Schweig, A. G. Anastassiou and J. C. Wetzel, Tetrahedron, **30**, 4089 (1974).

(6) Entirely consistent spectroscopic (IR, ^{1}H-NMR, ^{13}C-NMR, UV, MS) and combustion (C,H,X) data were obtained for all new compounds prepared. Of the various new substances listed in the table, **3b**(mp.137-139°C), **3d**(mp.238-240°C), **5b**(mp.154-156°C) and **5d**(mp.198-200°C) are solids while **3a**(ν_{NH}^{neat} 3110 cm^{-1}) and **5a**(ν_{NH}^{neat} 3100 cm^{-1}) are liquids.

(7) A. G. Anastassiou, J. Am. Chem. Soc., **90**, 1527 (1968).

(8) L .A. Paquette, U. Jacobsson and M. Oku, Chem. Commun., 115 (1975).

(9) Especially noteworthy in this connection is (i) the consistent correspondence, within each member, between key differences in energy and J_{CH} "exaltations" (parenthesized values which is entirely in keeping with the phenomenon of bicycloconjugation and (ii) the intermediate position occupied by the parent in this sequence which is clearly dismissive of any alternate explanation based on "annulation" effects.

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