Heterohomoconjugation in the 2-Azabicyclo[3,2,1]octa-3,6-diene System

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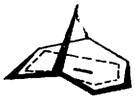
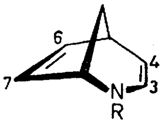
Summary Evidence based on ^{1}H n.m.r., ^{13}C n.m.r. and u.v. spectroscopy is presented for the existence of homoconjugation in the title heterobicycle.

Despite much work[1] on non-bonded π-interactions in carbobicyclic compounds, the role of heteroatomic lone pairs in non-classical properties such as heterohomoconjugation and heterobicycloconjugation has received little attention.[2] We have examined the possible occurrence of nonbonded π effects in the title system (**2**), namely the aza analogue of carbanion (**1**), a well studied homoconjugated carbobicycle.[3]



(1)



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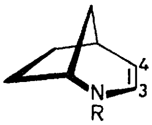

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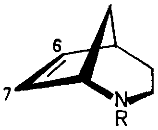

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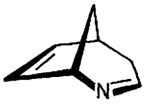
a, R = CN
b; R = CO_2Me
c; R = Me



(5)

The cyanoamide (**2a**) was prepared as described previously,[4] the methyl carbamate (**2b**) was formed by a similar ring expansive addition with norbornadiene and methyl azidoformate instead of N_3CN, and the *N*-methyl derivative (**2c**) was prepared by treatment of (**2b**) with $LiAlH_4$.† The partially saturated derivatives of (**3**) were synthesized by di-imide reduction of their dehydro analogues (**2**). The cyanoamide (**4a**) and the methyl carbamate (**4b**) were obtained on treatment of (**5**) [prepared by consecutive exposure of (**2b**) to MeLi and H_2O]‡ with $LiAlH_4$ and then cyanogen bromide and methyl chloroformate respectively; exposure of (**4b**) to $LiAlH_4$ gave the *N*-methyl derivative (**4c**).

TABLE 1. Selected ^{1}H n.m.r. signals of (**2a**), (**2c**), (**3a**), (**3c**), (**4a**), and (**4c**)

Compound	Proton[a]				
	3-H	4-H	6-H	7-H	Me
(**2a**)	4·30	4·80	3·71	4·36	—
(**3a**)	4·15	4·82			—
(**4a**)			3·73	4·06	—
(**2c**)	4·71	5·37	4·00	4·95	7·28
(**3c**)	4·60	5·40			7·48
(**4c**)			3·98	4·25	7·95

[a] Chemical shifts in τ units; all determinations for *ca.* 1·1mM CCl_4 solution.

The potentially homoconjugated azadienes (**2**) and models (**3**) and (**4**) were compared by n.m.r. and u.v. spectroscopy.

The ^{1}H n.m.r. data in Table 1 show that the two π segments of (**2**) do interact with net transfer of lone pair density [0·2 p.p.m. downfield shift of methyl resonance from (**3c**) to (**2c**)] into the ethylene bridge [0·7 p.p.m. upfield shift of the 7-H resonance from (**4c**) to (**2c**)]. As expected, this non-bonded transfer of lone pair density occurs less readily in the cyanoamide (**2a**), the corresponding upfield shift of 7-H§ being here only 0·3 p.p.m. [$<\frac{1}{2}$ that observed with (**2c**)].¶ The appropriate ^{13}C n.m.r. shifts, which more directly reflect changes in electron density, established that both carbon atoms of the formally isolated ethylene group experience an increase in electronic charge. Specifically, the C-6 and C-7 resonances undergo upfield shifts of 2·8 and 8·1 p.p.m. respectively on passing from (**4c**) to (**2c**); upfield shifts of 6·3 and *ca.* 0 p.p.m. were also recorded for C-4 and C-3, respectively, on changing the molecular environment from (**3c**) to (**2c**).

TABLE 2. U.v. spectra of (**2a**—**c**) and (**3a**—**c**) (solutions in n-hexane).

Compound	λ_{max}/nm (ϵ)
(**2a**)	233 (6000); 250 (3600)
(**3a**)	225 (2250)
(**2b**)	222 (5670); 249 (5700)
(**3b**)	230 (14,000)
(**2c**)	242 (2470); 272 (1350)
(**3c**)	248 (1950)

The u.v. spectra of (**2a**—**c**) and (**3a**—**c**) (Table 2) also provide strong indication of non-bonded interaction between the two formally isolated chromophores. The single band from the partially saturated derivatives (**3**) changes into two well defined maxima on passing to the dehydro analogues (**2**), the relatively low energy (250—272 nm) of the new band establishing that the remote double bond does not operate in isolation but is strongly coupled to the enamine group.

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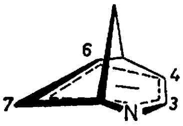
† All new compounds were subjected to full spectral (i.r., u.v., n.m.r., m.s.) characterization.

‡ The ready formation of (**5**) under these conditions has, to date, frustrated all efforts to synthesize the parent azadiene, (**2**; R = H).

§ The 6- and 7-H resonances in the n.m.r. spectrum of (**2**) were assigned by direct analogy with earlier designations relating to the spectrum of 2-oxabicyclo[3,2,1]octa-3,6-diene (M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, 1965, **48**, 1985).

¶ An interesting member of this series is the amide (i) which was detected (n.m.r.), but not isolated pure, several times in the treatment of compound (**2b**) with MeLi. It shows the following key n.m.r. resonances: τ (60 MHz; $[^{2}H_{8}]$tetrahydrofuran) 4·22 (d, 3-H), 4·98br (d, 6-H), and 5·73br (d, 7-H). The substantial upfield shift of 6-H (0·98 p.p.m.) and 7-H (0·78 p.p.m.) relative to (**2c**) reflects an increase in the electron density of the remote ethylene segment with increasing availability of the nitrogen lone pair, while the downfield shift of 3-H relative to (**2c**) (0·49 p.p.m.) parallels the situation with the carbanion (**1**).[3b]



(i)

The combined spectral information allows classification of (**2**) as a heterohomoconjugated system.

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[1] For a critical discussion see: S. Winstein, 'Chemical Society International Symposium on Aromaticity,' Sheffield, July 6—8, 1966; Special Publication No. 21, The Chemical Society, London, 1967; M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, 1971, **93**, 6193.

[2] For recent photoelectron spectroscopic investigations see: H. Schmidt, A. Schweig, A. G. Anastassiou, and H. Yamamoto, *J.C.S. Chem. Comm.*, 1974, 218; C. Muller, A. Schweig, A. G. Anastassiou, and J. C. Wetzel, *Tetrahedron*, 1974, **30**, 4089.

[3] (a) J. M. Brown and J. L. Occolowitz, *Chem. Comm.*, 1965, 376; (b) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, 1967, **89**, 3656.

[4] A. G. Anastassiou, *J. Org. Chem.*, 1966, **31**, 1131.