

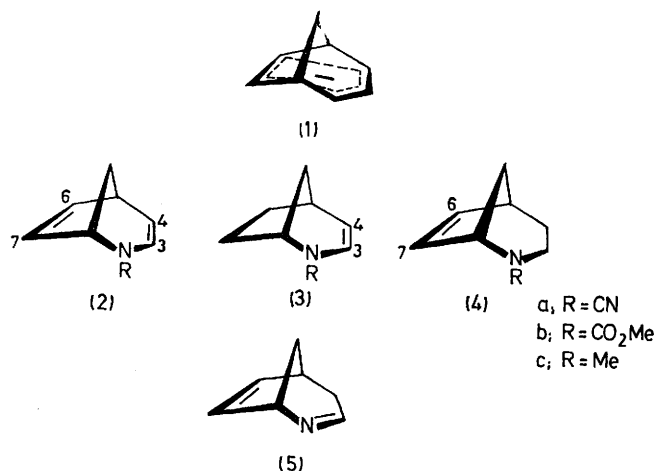
Heterohomoconjugation in the 2-Azabicyclo[3,2,1]octa-3,6-diene System

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Summary Evidence based on ^1H 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 work¹ on non-bonded π -interactions in carbobicyclic compounds, the role of heteroatomic lone pairs in non-classical properties such as heterohomocon-

jugation 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 carbobicyclic.³



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 N₃CN, and the *N*-methyl derivative (2c) was prepared by treatment of (2b) with LiAlH₄.[†] 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

TABLE 1. Selected ¹H 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

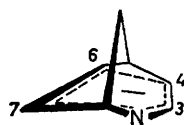
^a Chemical shifts in τ units; all determinations for *ca.* 1.1mm CCl₄ solution.

[†] 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; [²H₆]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}

obtained on treatment of (5) [prepared by consecutive exposure of (2b) to MeLi and H₂O][‡] with LiAlH₄ and then cyanogen bromide and methyl chloroformate respectively; exposure of (4b) to LiAlH₄ gave the *N*-methyl derivative (4c).

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

The ¹H 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 δ being here only 0.3 p.p.m. [$< \frac{1}{2}$ that observed with (2c)].[¶] The appropriate ¹³C 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.

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. Ocolowitz, *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.