

Photoelectron Spectroscopic Evidence for Bicycloconjugation in 9-Azabicyclo[4,2,1]nona-2,4,7-triene

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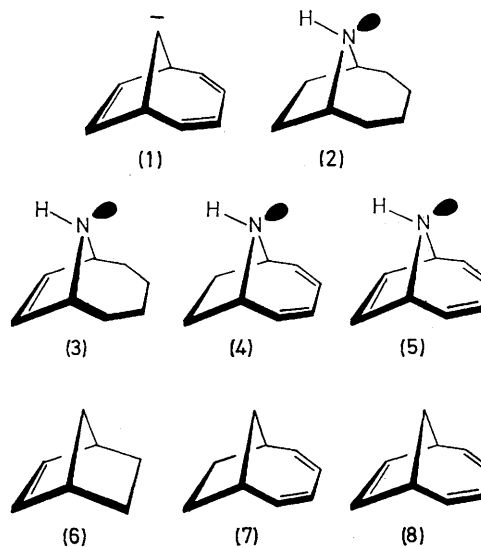
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Summary Photoelectron spectroscopic evidence supports the existence of bicycloconjugation (interaction between *all* formally isolated π segments) in 9-azabicyclo[4,2,1]nona-2,4,7-triene (5).

THE bicyclic carbanion (1) has recently been predicted¹ to be bicycloaromatic² on the assumption that its framework enables conjugative interaction between all three of its formally isolated π segments, *i.e.*, bicycloconjugation. We now offer evidence based on photoelectron (p.e.) spectroscopy that the iso- π -electronic heterobicycle, 9-azabicyclo[4,2,1]nona-2,4,7-triene,³ is in fact a bicycloconjugated molecule.

In order to distinguish between bicycloconjugation and the more localized process involving interaction between any two of the three π segments of (5), we recorded the p.e. spectra of the model compounds (2),⁴ (3),⁴ and (4)³ as well as that of (5). These substances are characterized by relatively sharp p.e. bands; (2): 8.50 eV (i); (3): 8.76 (i) and 9.17 eV (ii); (4): 8.36 (i), 8.64 (ii), and 10.73 eV (iii); and (5): 8.45 (i) + (ii), 9.39 (iii), and 11.17 eV (iv).



Band assignments in the spectra of (3), (4), and (5) were made on direct comparison with the spectrum of (2) in conjunction with those of (6), (7),⁵ and (8), respectively.† Band (i) in the spectrum of (2) is necessarily due to ionization from the orbital containing the nitrogen lone pair (n_s). Bands (i) and (ii) in the spectrum of (3) must then be ascribed to ionization from n_s and the ethylenic π (π_{2s}) MO [in (6), π_{2s} is located at 8.97 eV⁶] respectively. By similar reasoning, bands (i), (ii), and (iii) in the p.e. spectrum of (4) must be associated with ionization from the highest occupied MO of butadiene π_{1a} [in (7), π_{1a} is located at 8.23 eV], n_s , and the lowest occupied butadiene π MO, π_{3s} [in (7), π_{3s}

is located at 10.46 eV], respectively. Finally, the three bands (intensity ratio *ca.* 2:1:1) in the spectrum of (5), (i) + (ii), (iii), and (iv) must be due to ionization from π_{1a} [in (8), π_{1a} is located at 8.36 eV⁷] and n_s (double band), π_{2s} [in (8), π_{2s} is located at 9.02 eV⁷], and π_{3s} [in (8), π_{3s} is located at 10.55 eV⁷], respectively.

Comparison of the measured orbital energies of compounds (2), (3), and (6) reveals the absence of conjugative interaction between n_s and π_{2s} of (3), both levels being stabilized (n_s by 0.26 eV and π_{2s} by 0.20 eV) relative to their counterparts in the model systems, through mutual inductive interaction. Moreover, comparison of the orbital energies of (2), (4), and (7) shows a similar situation in (4), whereby all π levels are stabilized under the inductive influence of the nitrogen bridge [π_{3s} lowered by 0.27 eV and π_{1a} by 0.13 eV relative to their counterparts in (7)] and the butadiene unit [n_s lowered by 0.14 eV relative to its counterpart in (2)].

The situation is radically different for (5) as depicted by the correlation diagram in the Figure. Here, MOs π_{3s} and π_{2s} are stabilized respectively by 0.62 and 0.37 eV relative to their counterparts in (8), the energy lowering in each case significantly exceeding that estimated on the basis of purely inductive interaction with the lone pair (n_s) *i.e.*, 0.27 eV for π_{3s} and 0.20 eV for π_{2s} . The extra stabilization of each level (0.35 eV for π_{3s} and 0.17 eV for π_{2s}) must then be due to its conjugative interaction with n_s .[‡] In accord with this interpretation the lone pair (n_s) is substantially destabilized by this combined interaction from 8.90 eV estimated on the basis of a purely inductive model [8.50 eV, energy of n_s in (2) + 0.14 eV, inductive stabilization of n_s in (4) + 0.26 eV, inductive stabilization of n_s in (3)] to 8.45 eV.

In summary, the strong conjugative coupling detected between all three formally isolated π segments of (5), when viewed in the light of the lack of such interaction between any two such fragments in (3), (4), and (8), establishes that the azabicyclotriene (5) is a bicycloconjugated molecule.

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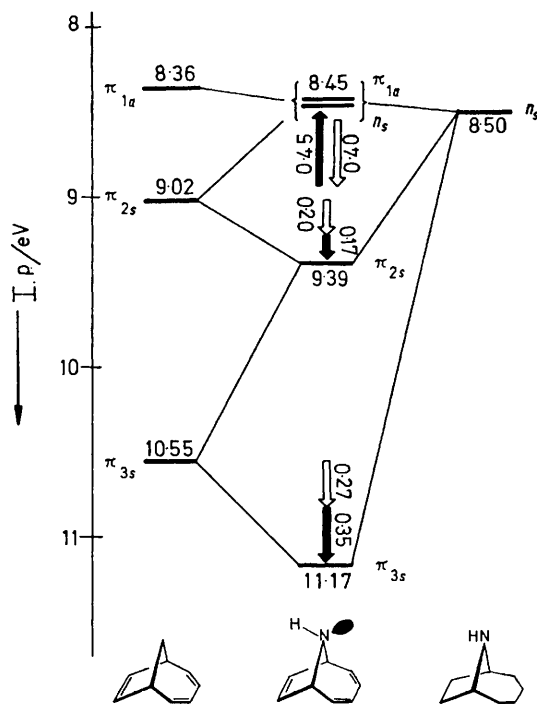


FIGURE. Correlation diagram of key occupied MOs of (2), (5), and (8). The unfilled and filled arrows represent the inductive and conjugative effects (eV), respectively. The numbers shown above or below the levels are vertical ionization potentials (eV). MOs are classified in terms of the molecular plane of symmetry (*s* = symmetric, *a* = antisymmetric).

† All band assignments receive support from the results of MINDO/2 calculations (M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969). The assumed correlation between band and orbital energies rests on the validity of Koopmans' theorem (T. Koopmans, *Physica*, 1933, 1, 104).

‡ According to CNDO/2 calculations (J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970) the isomer with the N-H bond over the two-carbon bridge is more stable than its invertomer by 10.3, 6.4, and 5.4 kcal/mol for (3), (4), and (5) respectively. These molecules must thus exist almost exclusively with the lone pair positioned *syn* to the C-4 segment of the skeleton. Nonetheless, the calculated isodensity contours relating to the lone pair show relatively high electron density on either side of the bridge. Consequently, interaction between lone pair and ethylene ought to be possible in (3) and (5) in spite of the predicted *anti*-disposition of the two groups in each case.

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