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HETEROHOMOCONJUGATION VERSUS HETEROBICYCLOCONJUGATION IN 9-THIABICYCLO[4.2.1]NONA-2,4,7-TRIENE[a]

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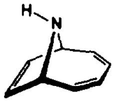
Abstract—The bridged heterocycles, 9-thiabicyclo[4.2.1]nonane (3), 9-thiabicyclo[4.2.1]non-7-ene (4), 9-thiabicyclo[4.2.1]nona-2,4-diene (5) and 9-thiabicyclo[4.2.1]nona-2,4,7-triene (2), were examined by photoelectron spectroscopy and the various MO levels theoretically located in each case by CNDO/S calculation. The combined information is best interpretable in terms of localized π interaction between sulfur and ethylene but not butadiene. The conclusion therefore is that thiabicyclotriene 2 is not a heterobicycloconjugated molecule but rather one best described as heterohomoconjugated.

INTRODUCTION

In a recent report[1] we presented evidence based on photoelectron spectroscopy that 9-azabicyclo-[4.2.1]nona-2,4,7-triene (1) is a heterobicycloconjugated molecule† in the sense that the occupied π MO's of both hydrocarbon appendages (ethylene and butadiene) and the nitrogen lone pair interact with one another. In an attempt to gain insight into the role of the heteroatom as a participant in bicycloconjugation and also to possibly expose the factors responsible for activation of this "closed-loop" interaction in preference to the more localized homoconjugative[3]‡ process, we undertook the photoelectron spectroscopic examination of the recently prepared[4] sulfur counterpart of **1**, namely 9 - thiabicyclo[4.2.1]nona - 2,4,7 - triene (**2**) and also of key variously saturated models§ **3**, **4** and **5**. The present report describes our findings and interpretations along these lines.



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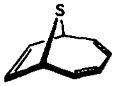

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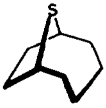

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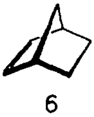

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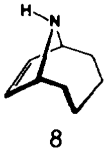

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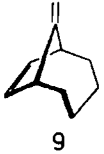

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[a] Part 50 of *Theory and Application of Photoelectron Spectroscopy*. For part 49 see Ref. 10.

† The term heterobicycloconjugation is employed here to denote a special type of bicycloconjugation[1] just as heteroconjugation characterizes a special category of conjugation. In other words bicycloconjugation is related to the well-known terms bicycloaromaticity and bicycloantiaromaticity[2] in the same sense as conjugation is to aromaticity and antiaromaticity.

‡ Current usage equates "homoconjugative" and "bicycloconjugative" interactions with "through space" and "hyperconjugative" interactions with "through bond" processes. In a recent paper [M. J. Goldstein and S. Natowsky, *J. Am. Chem. Soc.* **95**, 6451 (1973)] it was recognized, however, that the aforementioned distinction between σ and π 1,3-interaction processes is, at least from an experimental point of view, not a practical one. In accord with this result we employ the term homoconjugation here to denote any observable 1,3-interaction irrespective of whether this interaction is due to a "through space" or a "through bond" process. The same sort of redefinition applies to the term bicycloconjugation.

§ The preparation and chemistry of these substances (J. C. Wetzel, Syracuse University) will be described in a subsequent report.

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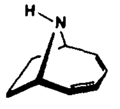

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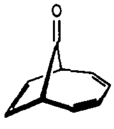

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Band assignments

The sharp well separated band in the PE spectrum* of fully saturated thiabicycle **3** (①= 8·16 eV), shown in Fig 1, is clearly associated with ionization of the isolated sulfur lone pair, the one perpendicular to the CSC bridge, and, within the validity of Koopmans' theorem,[5] denotes the key location of the highest occupied n_s† orbital in the absence of π perturbation. As expected, the PE spectrum of the dehydro analog **4**, depicted in Fig 2, contains two well resolved bands at low energy, ①= 8·20 eV and ②= 9·28 eV, the narrower of which exhibits the type of sharpness one normally associates with ionization from a nonbonding level; it follows then that band ② arises from expulsion of a $\pi_{2,S}$ ethylenic electron ($\pi_{2,S}$ of model, **6**, is located at 8·97 eV[6]). Notably, this level assignment, based on band shape, receives full support from the results of an all-valence electron calculation by the extended CNDO/S method[7] which place the n_s level of **4** some 0·7 eV *above* its $\pi_{2,S}$ counterpart (see calculated portion of level diagram in Fig 3). In the PE spectrum of the corresponding diene **5** (Fig 4) one readily discerns three low energy sharp bands, as expected. These are assigned as follows: ①= 8·26 eV (n_s), ②= 8·59 eV ($\pi_{4,a}$) and ③= 10·51 eV ($\pi_{4,S}$). Judging from the position of $\pi_{4,S}$ in model diene **10** (10·46 eV)[1] the assignment of band ③ to its counterpart in **5** appears to rest on secure ground. On the other hand, because of close energy similarities the specific assignments of bands ① and ② might, at first glance, be regarded as tenuous. Nonetheless, closer examination reveals this to be the *only* reasonable assignment insofar as its reversal, i.e., ① associated with $\pi_{4,a}$ and ② with n_S, would lead to the impossible situation whereby n_s of **3** is strongly stabilized (by 0·43 eV) on passing to its counterpart in **5**, while both π levels of the butadiene portion remain essentially unchanged on going from **10** to **5**. Further, the proposed assignments are fully consistent with the ordering of levels obtained from theory, shown in the calculated level diagram of Fig 5. Finally, the PE spectrum of triene **2**, shown in Fig 6, is seen to fulfill the expectation of four low energy bands. For reasons already advanced in connection with the spectra of **3**, **4** and **5** the most reasonable assignment here is ①= 8·39 eV (n_S), ②= 8·65 eV ($\pi_{4,a}$), ③= 9·33 eV ($\pi_{2,S}$) and ④= 10·66 eV ($\pi_{4,S}$). Again the proposed ordering of levels (Fig 7) is fully supported by theory.

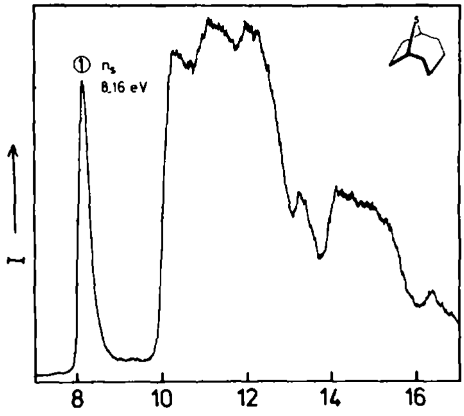

Fig 1. Photoelectron spectrum of 9-thiabicyclo[4.2.1]nonane (3) with assignment. The number associated with the band denotes vertical ionization potential in eV.

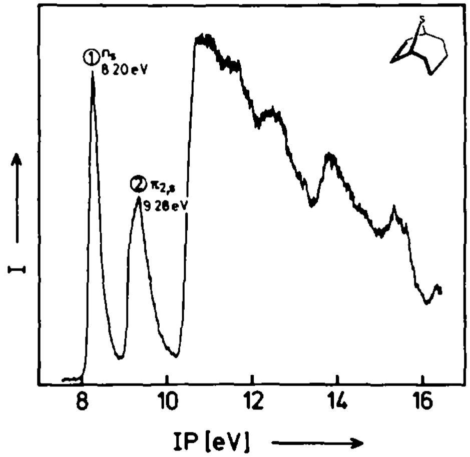

Fig 2. Photoelectron spectrum of 9-thiabicyclo[4.2.1]nona-7-ene (4) with assignments. The numbers associated with the band denote vertical ionization potentials in eV.

Interpretation

Before attempting an interpretation of the present results it would, perhaps, be instructive to briefly review the types of nonbonded π interac-

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*The HeI (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England).

†The MOs are classified in terms of the π segment (2 = ethylene, 4 = butadiene) on which they are mainly localized and in terms of the molecular plane of symmetry (s = symmetric, a = anti-symmetric).

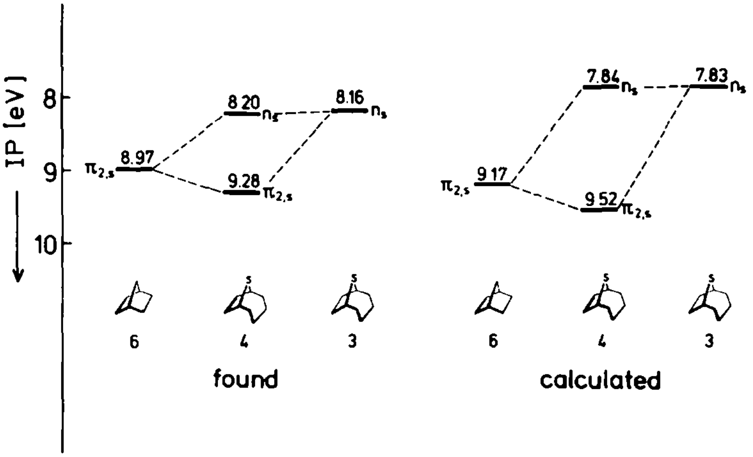

Fig 3. Observed and calculated (CNDO/S) level diagrams correlating key occupied MO's of norbornene (**6**) and 9-thiabicyclo[4.2.1]nonane (**3**) with those of 9-thiabicyclo[4.2.1]non-7-ene (**4**). The numbers denote vertical ionization potentials in eV.

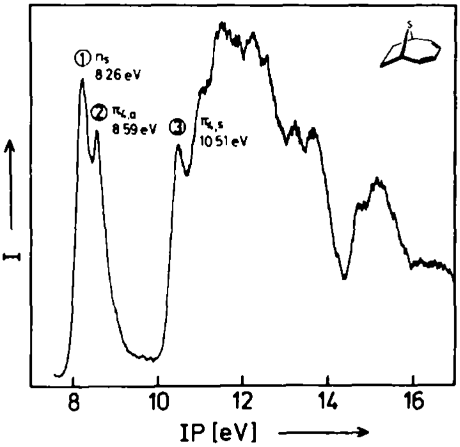

Fig 4. Photoelectron spectrum of 9-thiabicyclo[4.2.1]nona-2,5-diene (**5**) with assignments. The numbers associated with the bands denote vertical ionization potentials in eV.

tions available to systems such as **1** and **2**. First, there is mutual inductive polarization of the interacting groups and second there is conjugative interaction. The two operate in fundamentally different ways, with the former being independent of molecular symmetry and invariably leading to stabilization of *all* π levels of the interacting groups and the latter adhering to the strict condition that only levels of the same symmetry be allowed to interact and leading either to stabilization or destabilization of a level depending on its location in the manifold of interacting orbitals. Pertinent examples in this connection are provided by (i) the strong homoconjugative interaction observed in 2,5-dihydrothiophene[8] where the $\pi_{2,S}$ level (located at 9·33 eV in the model) is stabilized by a substantial 0·53 eV while n_S (located at 9·09 eV in the model) undergoes equally impressive (0·55 eV) destabilization and (ii) the mutual inductive polarization between nitrogen lone pair and ethylene observed in **8**[1] which results in significant stabilization of *both* levels (0·26 eV for n_S and 0·20 eV for $\pi_{2,S}$); similar inductive lowerings of the upper level have also been observed in 9-methylenebicyclo[4.2.1]nona-7-ene (**7**)[9] and bicyclo[4.2.1]nona-2,4,7-trien-9-one (**12**).[10]

Bearing all these points in mind, we now turn to the interpretation of the present results. First, in the case of **4** we note (Fig 3) that while $\pi_{2,S}$ is strongly stabilized (by 0·31 eV) relative to its counterpart in the model (**6**), n_S remains essentially invariant on passing from **3** to **4**. Now, since the stabilization of $\pi_{2,S}$ must be due to its interaction with n_S, the only higher-energy occupied orbital available to the molecule, it follows that the failure of n_S to undergo change from **3** to **4** must be due to the fortuitous cancellation of opposing conjugative (destabilizing) and inductive (stabilizing) effects. There is then homoconjugative interaction between lone pair and ethylene in **4**. Moreover, the CNDO/S[7] calculation places the bonding $\pi_{2,S}/n_S$ combination above its antibonding counterpart, suggesting that the homoconjugative process is due to hyperconjugative interaction. In **5** (Fig 5) it is the lowest π level ($\pi_{4,S}$) which remains essentially invariant relative to its counterpart in **10**, while both $\pi_{4,a}$ and n_S are stabilized. The insensitivity of $\pi_{4,S}$ to the introduction of the sulfur bridge clearly denotes lack of interaction between this level and n_S, and since $\pi_{4,S}$ is the only filled π level of **5** to possess proper symmetry for conjugative interac-

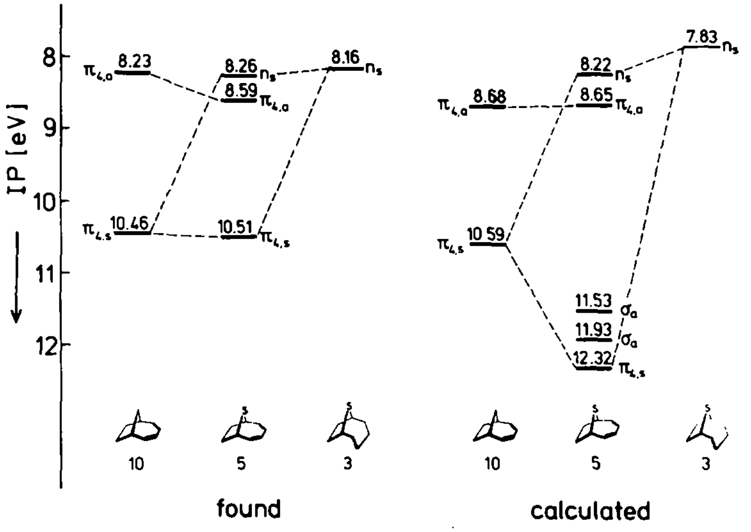

Fig 5. Observed and calculated (CNDO/S) level diagrams correlating key occupied MO's of bicyclo[4.2.1]nona-2,4-diene (**10**) and 9-thiabicyclo[4.2.1]nonane (**3**) with those of 9-thiabicyclo[4.2.1]nona-2,4-diene (**5**). The numbers denote vertical ionization potentials in eV.

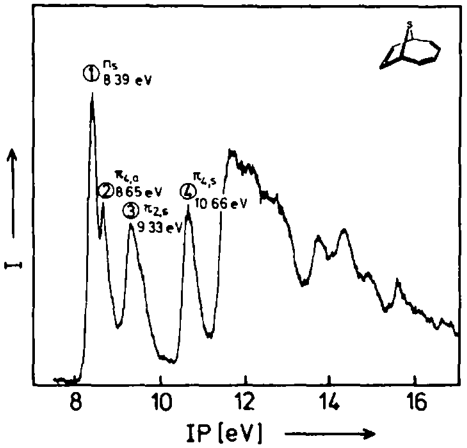

Fig 6. Photoelectron spectrum of 9-thiabicyclo[4.2.1]nona-2,4,7-triene (**2**) with assignments. The numbers associated with the bands denote vertical ionization potentials in eV.

tion with the lone pair, it follows that the molecule (**5**) is not endowed with a homoconjugated frame. Finally, brief inspection of the PE spectrum of triene **2** reveals that it is largely a composite of those of **4** and **5**. It is seen for instance, that here too, as in the case of diene **5**, $\pi_{4,S}$ remains virtually invariant relative to its analog in the model (**13**),[11] $\pi_{2,S}$ is stabilized by the same amount (0·31 eV) as its counterpart in **4** and n_S and $\pi_{4,a}$ are both stabilized in the manner noted earlier for **5**. It follows that the major inter-group conjugative process operating in **2** is homoconjugative interaction between lone pair and ethylene. In other words, the molecule does not possess a bicycloconjugated frame but rather one best described as heterohomoconjugated.*

In concluding we should like to stress the striking contrast between **2** and its nitrogen relative shown in **1**, which was recently shown to possess well developed bicycloconjugation. Now, while **1** and **2** do differ in structural detail such as the "size" of the heteroatom and the length and strength of the C–X bond, brief comparison of these two relatives in terms of MO energetics immediately reveals that the observed differences in nonbonded conjugation may be due, in large measure, to differences in heteroatom electronegativity. Within this line of reasoning, the bicycloconjugative potential of **2** fails to materialize chiefly because of the relatively large energy (2·39 eV) separating the two extreme levels of like symmetry, n_S and $\pi_{4,S}$. In **1**, on the other hand, where the greater electronegativity of nitrogen, compared to sulfur, reduces the difference between the same two levels to 2·05 eV,[1] interaction between isosymmetric extremes is possible leading to the development of extensive bicycloconjugation. Interestingly, the requirement set by heteroatom electronegativity for the development of bicycloconjugation in **1** and **2**, i.e., increased electronegativity allowing for improved energy matching and thus more effective conjuga-

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*The term heterohomoconjugation is used to describe homoconjugation[4] between MO's of π segments and those localized on heteroatoms.

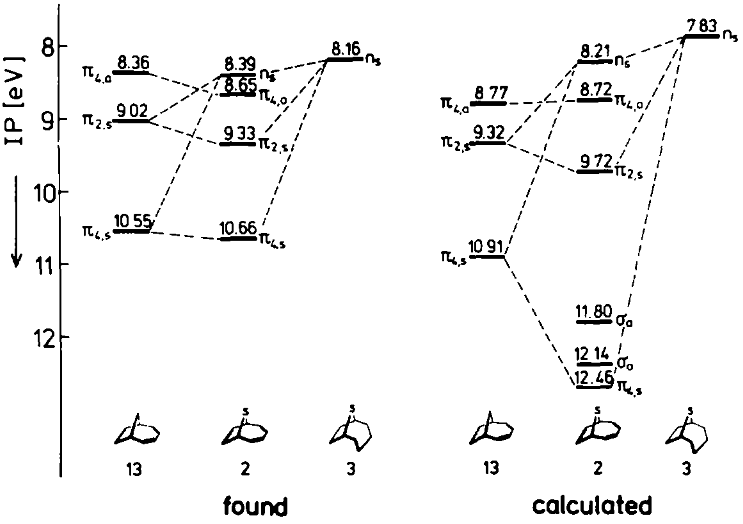

Fig 7. Observed and calculated (CNDO/S) level diagrams correlating key occupied MO's of bicyclo[4.2.1]nona-2,4,7-triene (2) and 9-thiabicyclo[4.2.1]nonane (3) with those of 9-thiabicyclo[4.2.1]nona-2,4,7-triene (2). The numbers denote vertical ionization potentials in eV.

tive interaction between n_S and $\pi_{4,S}$, is seen to be the exact reverse of that controlling the more conventional heteroconjugative process among the monocyclic analogs, the hetereonins,[12] where the affinity of the heteroatom lone pair to delocalize into the π system is well known to increase with reduced effective electronegativity.

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