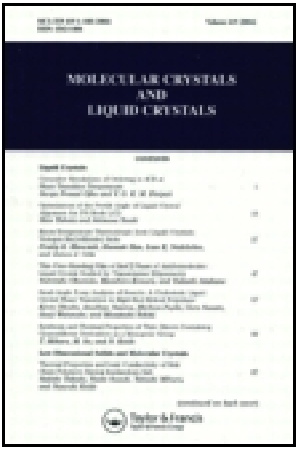

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Π-Conjugated Non-Kekule Molecules and the Limits of Hund's Rule

Jerome A. Berson [a]
[a] Department of Chemistry, Yale University, New Haven, Connecticut, 06511

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Π-CONJUGATED NON-KEKULE MOLECULES AND THE LIMITS OF HUND'S RULE.

JEROME A. BERSON
Department of Chemistry, Yale University, New Haven, Connecticut 06511.

Abstract Whether certain theoretical restrictions on the applicability of Hund's rule must be kept in mind for the proper design of high-spin organic molecules as potential building blocks for ferromagnetic materials is a subject of intense current concern. It has been almost fifty years since E. Hückel pointed out that a biradical constituted by union of inactive sites of two monoradicals might have a singlet ground state. Experimental tests of this conjecture (in its recent more sophisticated formulations by Borden and Davidson and by Ovchinnikov) now have led to the synthesis and characterization of several new ground state singlet biradicals.

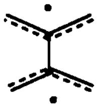
INTRODUCTION

The effective design of high-spin organic materials by the combination or clustering of radical structures requires not only that due care be taken to prevent the mutual annihilation of the spins by chemical reaction but also that the connectivity pattern be appropriate for the application of Hund's rule.[2,3] That certain structures might violate the latter requirement was foreshadowed in a remarkable paper of E. Hückel in 1936.[1] Hückel showed that in a disjoint[4] biradical (mentally) constructed by union of two monoradicals at inactive sites (where the Hückel NBMO coefficients are zero), the exchange energy and hence the energy separation between the singlet and triplet states vanishes. This result contained the implication that the preference for the triplet should be much diminished or even reversed in disjoint systems. Modern electronic structure theory[4,5] generalized and greatly extended this argument, but fifty years intervened before experimental tests of the disjoint conjecture were set in motion.

Both semi-empirical and ab initio quantum mechanical calculations project an actual preference for the singlet in the disjoint hydrocarbon biradicals tetramethyleneethane (TME) **1**[4-6] and 1,2,4,5-tetramethylenebenzene **2**[6-8] (TMB) (see Figure 1). Electron spin resonance (ESR) observations of linear Curie law behavior of signals assigned to both species **1**[9] and **2**[10] have been interpreted as indicative of triplet ground states, but since this technique is incapable of distinguishing a singlet-triplet gap of 0.1 kcal/mol from one of 10 kcal/mol,[3] the results do not address directly the question of whether the disjoint conjecture is correct. It is a historical accident that, at the moment, the limitations of experiment essentially force one to find a clear violation of Hund's rule in order to establish the occurrence of the predicted major diminution of the triplet preference.

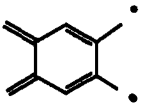
We hope to contribute to the question of the ground state of **2** in future publications, but in the present work, our efforts are directed toward the development of heterocyclic derivatives (**3a-c**) of **1**, a series of molecules we believe might be used ultimately to adjust the magnitude of the singlet-triplet gap almost at will. Our strategy is to introduce a perturbation sufficient to produce a Hund's rule violation and then to modify the structure gradually through a series of derivatives so as to restore high-spin hegemony. The perturbation is depicted in Figure 2, where the symmetry-allowed mixing of the symmetric component of the TME NBMOs with the heteroatom lone-pair orbital splits the nominal NBMO degeneracy.[9] This in turn should selectively stabilize the singlet in configurational interaction. The amount of the splitting will depend upon the overlap integral of the p and ψ_S orbitals and upon their energy separation.

TME SERIES



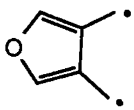
1

0.5 (INDO/S-CI)[a]
1.7 (SVP, SD-CI)[b]
1.4 (AM1/UHF)[e] $S^2 = 1.5, 2.3$
1.5 (AM1/CI)[e]



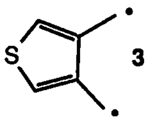
2

9.0 (INDO/S-CI)[d]
7.4 (SDTQ-π-CI)[d]
5.0 (SD-CI)[g]



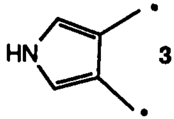
3a

0.5, 0.6 (INDO/S-CI)[a,d]
2.3 (SVP, SD-π-CI)[c]
6.4 (AM1/UHF)[e] $S^2 = 1.4, 2.3$
4.8 (AM1/CI)[e]



3b

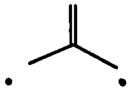
0.4 (INDO/S-CI)[d]
6.2 (AM1/UHF)[e] $S^2 = 1.4, 2.3$
4.8 (AM1/CI)[e]



3c

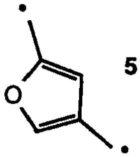
4.3 (INDO/S-CI)[d]
6.8 (SVP, SD-π-CI)[c]
9.1 (AM1/UHF)[e] $S^2 = 1.3, 2.3$
9.8 (AM1/CI)[e]

TMM SERIES



4

-11.1 (INDO/S-CI)[a]
-15.2 (MCSCF)[f]
-15.4 (AM1/UHF)[e] $S^2 = 1.1, 2.2$
-14.0 (AM1/CI)[e]

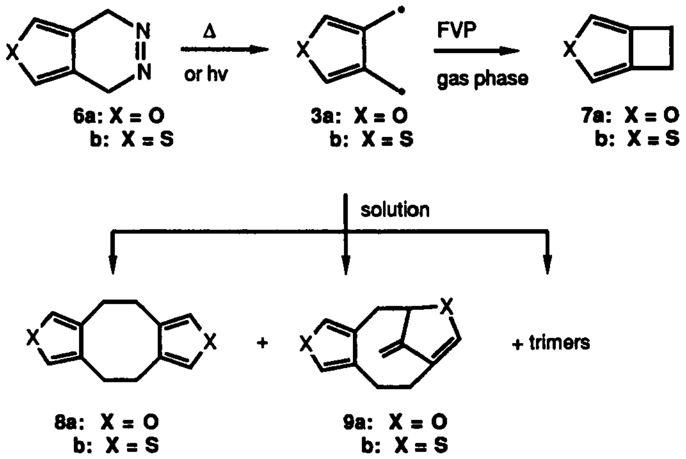


5

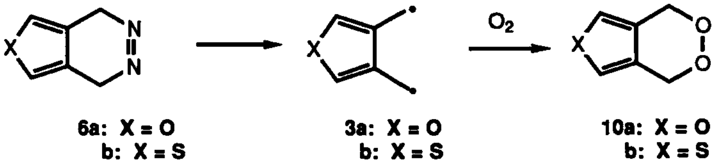
-13.3 (INDO/S-CI)[a]
-9.8 (AM1/UHF)[e] $S^2 = 1.3, 2.4$
-9.8 (AM1/CI)[e]

Figure 1. Calculated energy separations ($E_T - E_S$, kcal/mol) of lowest singlet and triplet states of biradicals.
[a]Ref. 6. [b]Ref. 4b. [c]Ref. 9. [d]Ref. 7. [e]Ref. 11. [f]Ref. 15. [g]Ref. 8.

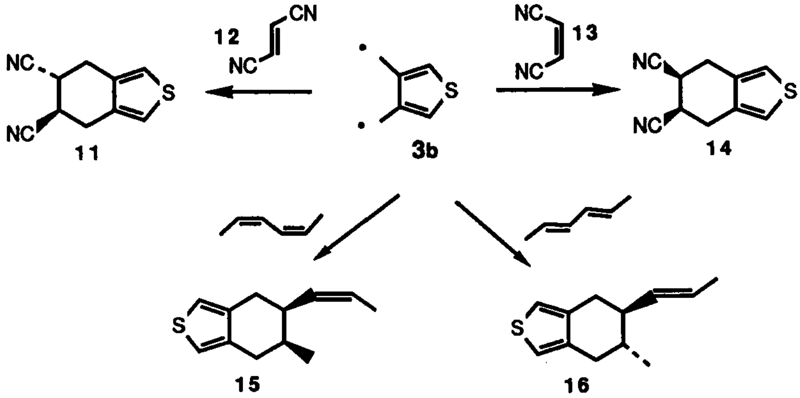
Scheme 1



Scheme 2



Scheme 3



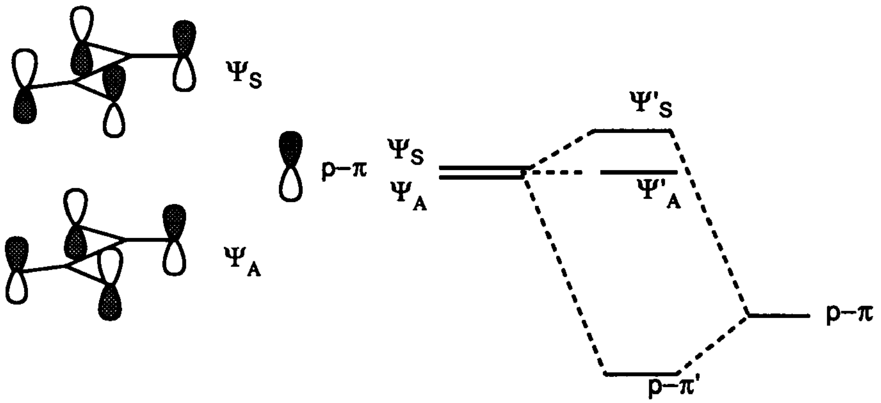


Figure 2. Perturbative interaction of filled heteroatomic p-π orbital with the NBMOs of tetramethyleneethane[9]

Figure 1 shows the results of quantum mechanical calculations on these structures. In accord with the qualitative predictions of the disjoint conjecture, the calculations show the diminution of the triplet preference expected in the heterocyclic series **3a-c** based on the disjoint hydrocarbon TME. In fact, singlet ground states are predicted in each case. On the other hand, note that the calculations also predict a large *triplet* preference for the non-disjoint hydrocarbon TMM (**4**) and its derived heterocycle **5**. This result supports the idea that the ordering of the spin states in these non-Kekulé molecules is crucially dependent upon connectivity.

CHEMICAL PROPERTIES OF 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE

Dimerization and Ring-closure (Scheme 1)

Thermal or photochemical decomposition of the furanodiazene **6a** in solution gives a symmetrical (**8a**) and an unsymmetrical (**9a**) dimer of 3,4-dimethylenefuran **3a**, in addition to small amounts of products whose empirical compositions correspond to trimeric materials. Similar reactions occur in the thiophene series generated from diazene **6b**.[11] Cyclobutane ring-closure products (*e.g.*, **7a** or **7b**) are not observed under these conditions, although they can be isolated in small yield from the flash-vacuum pyrolysis. These observations as well as others[12] provide support for previous suggestions[12-17] that **3a** and **3b** can be generated from other precursors.

Capture by Dioxygen and by Alkenes (Schemes 2 and 3)
Thermal decomposition of the diazenes **6a** or **6b** in the presence of O_2 leads to high yields of the bicyclic peroxides **10a** or **10b**(Scheme 2).[11] On the other hand, when a deoxygenated solution of **6a** or **6b** containing a suitable alkene (*e.g.*, **12** or **13**) is kept, cycloaddition products are formed (*e.g.*, **11** or **14**) The cycloaddadditions are highly stereospecific (>99.5%) syn processes. In the thiophene series shown, the regiochemistry is specifically fused, although both bridged and fused adducts are formed in the furan series. The product proportions are insensitive to the concentration of the trapping alkene, an observation that is consistent with only one reactive intermediate. That the cycloadditions are the result of sequential unimolecular and bimolecular steps, as indicated in Schemes 2 and 3, is demonstrasted by kinetic studies, which find the rate of disappearance of the diazenes to be independent of the concentration of the trapping agent.[11] The stereospecificity of the reactions is consistent with a singlet assignment to the capturable intermediate, although it does not prove the spin of the ground state.

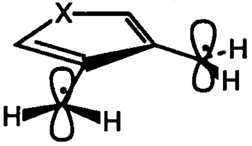
UV-VISIBLE SPECTROSCOPIC OBSERVATION OF 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE

Irradiation[11] of frozen solutions of diazenes **6a** or **6b** at 77 K results in rapid appearance of an intense purple color associated with the biradicals **3a**, λ_{max} = 560 nm, ε = 5.3×10^3 $M^{-1}cm^{-1}$, λ_{max} = 338, 348, and **3b**, λ_{max} = 568-572 nm, ε = 5.1×10^3 $M^{-1}cm^{-1}$. A direct correlation of the carriers of these spectra with the species responsible for the solution phase chemistry results from time-resolved spectroscopy of the transients generated by nanosecond flash photolysis. These species have the same absorption spectra as those observed in the solid matrices, and the relative rates of their disappearance in the presence of alkene trapping agents are the same as those observed in preparative competition experiments.[12]

THE BARRIER TO RING-CLOSURE IN 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE

Specimens of the two biradicals **3a** and **3b** in poly(methyl methacrylate) can be prepared by irradiation of films of the vehicle impregnated with one of the diazenes **6a** or **6b**. The characteristic purple colors and UV-VIS spectra of the biradicals remain at undiminished intensity for hours up to the softening point of the matrices, above 210 K. This means that there is an activation energy of at least 20-25 kcal/mol opposing the internal cyclization to the cyclobutanes**7a** or **7b**. The exact height of the barrier is not known, although the threshhold temperature for cyclization probably lies somewhere above the 210 K lower limit necessitated by the present matrix immobilization experiments and below the >550 K flash vacuum pyrolysis temperature used to obtain the cyclobutanes (Scheme 1).

Since radical-radical dimerizations occur at nearly every encounter, it seems at first glance incredible that two spin-paired radical sites in close proximity should resist immediate combination to form cyclobutanes **7a**/**7b**. The retardation in rate probably is caused by the necessity to twist the exocyclic methylene groups out of the plane of the furan or thiophene ring en route to the transition state for ring closure, thereby sacrificing some of the 20 kcal/mol of stabilization associated with two allylic systems of **3a**/**3b**.



3a: X = O
b: X = S

IN SEARCH OF THE ESR SPECTRA OF 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE

No such spectra have yet been seen. Intensely purple frozen solutions of **3a** or **3b** in 2-methyltetrahydrofuran (MTHF) were examined over the temperature range 12-80 K, and poly(methyl methacrylate) preparations of **3b** were studied up to 223 K, but no ESR signals attributable to a triplet species were detected, even though the samples contained > 5 x 10^{14} diyl molecules. Had (twice) this many unpaired spins been present as a consequence of a triplet ground state, they would have exceeded the probable limit of sensitivity of the ESR spectrometer by a factor of more than 10^3. If thermal equilibrium was achieved in this system, and if the failure to observe an ESR signal is caused by insufficient population of the triplet state rather than by rotationally induced uncertainty broadening or other spectroscopic complications, the temperature and spectrometer sensitivity can be used to deduce a minimum value of about 4.5 kcal/mol for the energy gap separating the ground state singlet from the triplet.

NMR SPECTRA OF 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE

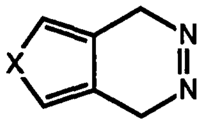
The failure to observe ESR spectra for biradicals **3a** and **3b**, although consistent with singlet ground states for these species, is a negative result. (For example, an alternative interpretation might place the blame upon lack of technical skill of the operators!) In a general way, this epistemological shortcoming could be overcome if one could identify an experiment that should give a *positive* response if the biradicals really were singlets. In principle, NMR spectroscopy satisfies this need, since the transitions of triplet biradicals would be contact-shifted by thousands of ppm and broadened by thousands of Hz because of the unpaired electron spins. Thus, only a singlet species should show unbroadened lines at normal chemical shifts, and the triplet should not be observable under ordinary conditions.

There is a difficulty, however, because the extremely short lifetime of these reactive species would preclude their observation in fluid media. The solution is to conduct the NMR spectroscopy on matrix-immobilized samples in the solid state. This is a daunting technical challenge, which has been met by Zilm's design and construction of a suitable probe insert for solid state ^{13}C NMR which permits magic-angle spinning at 2 KHz under conditions of cross polarization while maintaining the sample at 77 K. At the present state of the art, this technique has insufficient signal-to-noise ratio for natural abundance work, and samples must be generated from isotopically enriched precursors.[18]

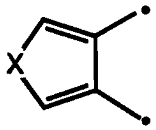
In this way, we have now observed unbroadened ^{13}C lines near 100-105 ppm for the transient purple species **3a** and **3b** generated from diazene **6a**[18a] and **6b**[18b] labeled in the CH_2 groups. Also, from diazene **6b** labelled in the 2- and 5-positions of the thiophene ring, we have observed a ^{13}C resonance for **3b** near 115 ppm.[18b] These chemical shifts are gratifyingly compatible with those expected of trivalent, sp^2-hybridized ^{13}C nuclei. Further two-dimensional spectra obtained with a modified separated local field technique[18c] has permitted the extraction of the H-C-H angle of the methylene groups of **3b** as 120°. These observations confirm the singlet nature of **3a** and **3b**.

CONCLUSIONS AND PROSPECTS

The qualitative ideas of the disjoint conjecture now have been confirmed by both theoretical calculations and by experiment. A variety of modern electronic structure computations have led to correct predictions of singlet ground states for 3,4-dimethylenefuran and 3,4-dimethylenethiophene. We have some confidence, therefore, that the predictions[7,9,11](Figure 1) of singlet ground states for 3,4-dimethylenepyrrole (**3c**) will be in accord with experiment. Very recently,[19] we have completed syntheses of the diazenes **6d-f**, and we hope soon to report on the properties of the corresponding biradicals **3d-f**. Changes in the electronic nature of the N-substituent in this series would be expected to raise or lower the energy of the nitrogen p-orbital and hence should permit us to "tune" the singlet-triplet gap (see Figure 2).



6



3

d: X = NCH_3
e: X = NCH_2Ph
f: X = $NSO_2C_7H_7$

ACKNOWLEDGMENTS

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