Recent studies of reactive intermediates. The limits of Hund's rule in pi-conjugated non-Kekulé molecules

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Abstract - Early as well as recent quantum theoretical insights suggest that disjoint non-Kekulé molecules should have singlet ground states, in violation of Hund's rule. Although this idea was first put forward fifty years ago, experiments to test it directly have been designed and carried out only recently. The disjoint bis-m-quinodimethanoid 6 has a triplet ground state, in contradiction to the qualitative theory. Detailed quantum calculations, however, suggest that compound 6 should have a triplet ground state, whereas 3,4-dimethylenefuran, 12, and 3,4-dimethylenethiophene, 13, heteroatom derivatives of the disjoint hydrocarbon tetramethyleneethane, should have singlet ground states. Very recent experiments are in accord with these predictions.
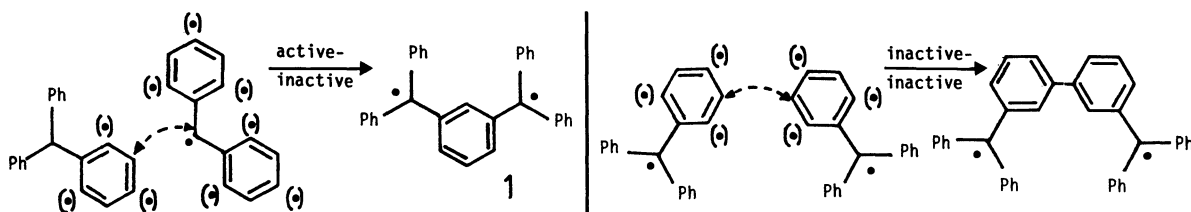
THEORETICAL INTRODUCTION

Non-Kekulé (ref. 1) π-conjugated molecules contain enough atoms but not enough bonds to satisfy the standard rules of valence (ref. 2). Nevertheless, a number of such compounds exist, and their properties, in some cases at least, are reasonably well understood.

One might imagine that Nature would impose a condign penalty on any rash enough to violate so basic a concept as the structural theory of organic chemistry. Indeed, the study of non-Kekulé molecules _is_ burdened with an unavoidable complexity, which originates in the need to specify the electronic spin state and configuration. However, in our view, this complexity stimulates rather than punishes. It motivates the search for predictability through an interplay of theory and experiment.

At a low level of theory, for example in the Hückel approximation, the pair of electrons from the (conceptually) broken bond of a non-Kekulé molecule occupy a degenerate pair of molecular orbitals (MOs). Because the available electrons suffice only to half-fill these orbitals, the Pauli principle permits three different schemes of occupancy: a "closed-shell" singlet (two electrons with paired spins in one orbital), an "open-shell" singlet (one electron in each orbital, with paired spins), and a triplet (one electron in each orbital, with unpaired spins). In these circumstances, it is customary (refs. 3-8) to invoke one version of Hund's rule, which states that the high-spin species will be favored. The physical basis of Hund's rule is the exchange energy, $\underline{K}$, which is most conveniently interpreted as an electrostatic term. The quantity $2\underline{K}$ is equal to the energy separation between the singlet and triplet (ref. 9).

Nevertheless, good theoretical reasons support the conjecture that Hund's rule may not apply to certain π-conjugated non-Kekulé molecules. This was first recognized by E. Hückel as long ago as 1936 (ref. 10) in a discussion of two non-Kekulé hydrocarbons of Schlenk and Brauns (refs. 11 and 12), 1 and 2. The connectivity patterns in the two molecules are fundamentally disparate. Because the carbon atoms at the 2-forming union have zero HMO coefficients (the sites are "inactive" (ref. 13)), the exchange energy vanishes at this level of approximation, and the normal basis for the application of Hund's rule vanishes with it.

For reasons that are not clear, Hückel's prescient paper of 1936 seems to have made little impact. Longuet-Higgins does not cite it in his very influential work of 1950 (ref. 14), and he makes no distinction between non-Kekulé molecules with inactive-inactive connections and those without. For example, he applies Hund's rule to predict triplet ground states for both tetramethyleneethane (3) and trimethylenemethane (4), which are the parent substances of the former and latter categories respectively.

In fact, more than forty years passed before attention was re-directed to the problem Hückel had addressed in 1936. The seminal papers are those of Borden and Davidson (ref. 15), Misurkin and Ovchinnikov (ref. 16), and Ovchinnikov (ref. 17). These theoretical studies have strengthened the conceptual basis for identifying which π-conjugated molecules might violate Hund's rule.
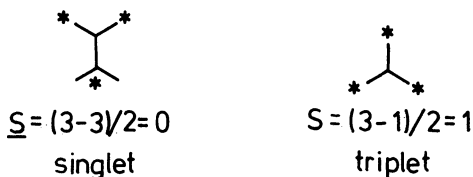
In the Borden-Davidson formalism, if the NBMOs are (or by linear combinations, can be) confined to separate regions of the molecule, they are said to be disjoint. This property, to first order, erases the Coulombic repulsion that usually destabilizes the singlet in π-conjugated biradicals.

Disjoint character is exemplified by the NBMOs of tetramethyleneethane (3a,b). This property of separability of the NBMOs means that, to first order, the peaks of the two electron distributions in the singlet state are as well separated as those in the triplet. This is to be contrasted with the more usual non-disjoint type of biradical, exemplified by trimethylenemethane, whose NBMOs (4a,b) cannot be confined to separate atoms by any linear combination.

At the SCF level of theory, the singlet and triplet states of a disjoint system are degenerate. A higher order effect, dynamic spin polarization, then can selectively stabilize the singlet and produce a violation of Hund's rule (refs. 18 and 19).
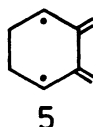
The formalism of Ovchinnikov (refs. 16 and 17) applies only to alternant systems. By treating such molecules with a Heisenberg Hamiltonian in a valence-bond theoretical framework, a formula for the total spin of the ground state for any alternant may be derived as half the difference between the number of starred and unstarred π-centers: $S = (n^* - n)/2$. Since the multiplicity is $2S + 1$, the Ovchinnikov spin formula predicts that in equal parity systems (where $n^* = n$), the ground state will be singlet. It has been shown (ref. 15) that such equal parity systems are disjoint, but that not all disjoint alternant systems have equal parity. Thus, the $S = 0$ cases of Ovchinnikov are a sub-category of disjoint molecules. How the spin formula works should be immediately obvious from the starring diagrams for tetramethyleneethane (3) and trimethylenemethane (4).

Note that the spin formula is proposed (ref. 17) to hold even in heteroatom perturbed π-conjugated systems, an assumption that is supported both computationally (ref. 20) and experimentally (refs. 2, 9d, and refs. cited therein) in the m-quinonoid series.
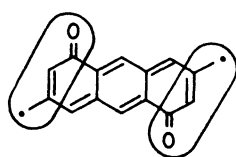
Although reasons to expect Hund's rule violations thus have been recognized for many years, Nature so far has frustrated attempts to verify these predictions. The obvious simple candidate, tetramethyleneethane (3) (ref. 21) tests the theory only if it exists in a planar geometry, but the weight of evidence is against this conformation (ref. 22). Similarly, the Schlenk-Brauns hydrocarbon 2 has been assigned a triplet ground state on the basis of the adherence of its EPR signal intensity to the Curie law (ref. 23). It seems probable that 2 is non-planar, so that its nominally equal-parity nature is not a reliable basis for predicting a low-spin ground state.

The tetramethyleneethane derivative 5 presumably is planar or nearly so, but the experimental evidence so far does not seem to permit an unequivocal assignment of the ground state (refs. 24 - 27).

5
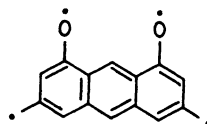
TESTS OF THE QUALITATIVE SPIN-RULE: TWO BIS-M-QUINOMETHANOIDS

The bis-m-quinomethanoid 6 constitutes a test of the equal-parity criterion for low-spin ground states (refs. 28 - 30). It is related to the simplest disjoint biradical tetramethyleneethane 3 in the sense that the Hückel NBMO electron density is confined to the two (ringed) pentadienyl moieties disjointly. The rigid conjugated framework prevents twisting about the connection between them. The isomeric molecule 7 is non-disjoint and formally a tetraradical, for which the spin formula predicts a quintet ground state. This species therefore serves as a control system to test the application of Hund's rule to a non-disjoint case that differs only in connectivity from the disjoint test case 6.

6

$$S = (9-9)/2 = 0$$

7
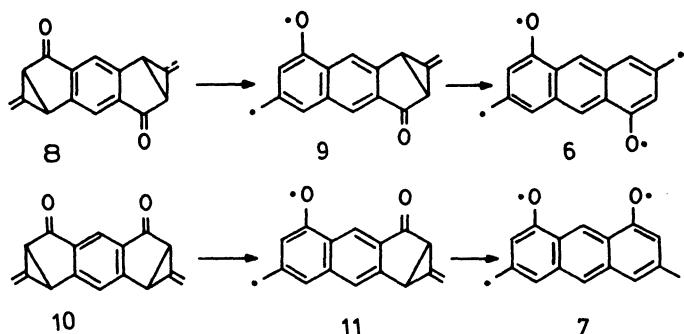
$$S = (11-7)/2 = 2$$

The syntheses of 6 and 7 are effected by successive photochemical ring-cleavages, 8 → 9 → 6, and 10 → 11 → 7, of samples immobilized in rigid media. The sequence of events can be monitored by both optical and EPR spectroscopy.

8   **9**   **6**

10   **11**   **7**

As expected, the control compound 7 has a quintet ground state. However, the equal-parity test compound 6 has a <u>triplet</u> ground state, rather than the theoretically anticipated singlet.

The apparent breakdown of the qualitative spin rules in the case of 6 makes it clear that other factors can sometimes override disjoint character. There can hardly be any doubt that the main idea of the qualitative theories is correct, namely that the exchange interaction of the SOMO electrons in equal-parity (therefore disjoint) π-conjugated non-Kekulé molecules is small, and hence that s singlet should be the ground state or a very low-lying excited state. The problem at present is to perceive the structural features of formally disjoint test molecules that act to restore some of the exchange coupling and thereby contaminate the desired pure test situation.
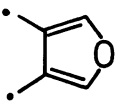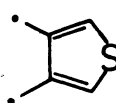
SEMIEMPIRICAL AND *AB INITIO* THEORETICAL SEARCHES FOR NEW LOW-SPIN NON-KEKULÉ MOLECULES

Accurate ab initio quantum chemical calculations on a molecule as large as 6 are impractical-
ly costly, at least for the present. However, one might hope to develop a semi-empirical
calculation that would confirm computationally the experimental observations in that case and
might serve as a guide to new low-spin non-Kekulé molecules. The INDO/S-CI method of Ridley
and Zerner (refs. 32a,b) has served well in this regard (ref. 20). Its utility has been es-
tablished by its ability to reproduce either ab initio calculations or experimental facts for
a number of non-Kekulé systems, and it may therefore be regarded as a calibrated semi-empiri-
cal method (ref. 20). In this context, it is encouraging to note the outcome of an INDO/S-CI
calculation (ref. 20) which places the triplet of the disjoint test system 6 4.3 kcal/mol
lower in energy than the singlet, in qualitative agreement with the experimental observations
of refs. 28 - 30.

PREDICTION AND EXPERIMENT IN THE 3,4-DIMETHYLENEFURAN AND 3,4-DIMETHYLENETHIOPHENE SYSTEMS

Analogous to the relationship of the m-quinonoids to benzene is that of the 3,4-dimethylene
derivatives 12 and 13 to the five-membered heterocyclic aromatics furan and thiophene. These
non-Kekulé substances are of special interest because the odd number of ring members makes
them non-alternant, so that Ovchinnikov's parity criterion for the spin of the ground state
does not apply. INDO/S-CI calculations (refs. 20 and 33) provide some insight into the
properties that might be expected of these substances and are supported by ab initio calcula-
tions (refs. 33 and 34). Some of the results are given in Table 1. The calculational
methods agree in predicting low-spin ground states for both species, which insofar as the
singlet-triplet splitting is concerned, may be considered to be minimally perturbed tetra-
methyleneethanes.

TABLE 1. Calculated energies of some non-Kekulé molecular states
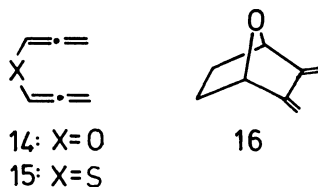
State	12		13	
	$^1A_1$	$^3B_2$	$^1A_1$	$^3B_2$
Rel. Energy, kcal/mol	0.0	0.5[a]	0.0	0.4[a]
	0.0	4.4[b]		
	0.0	1.7[c]		

[a] INDO/S-CI, ref. 20.
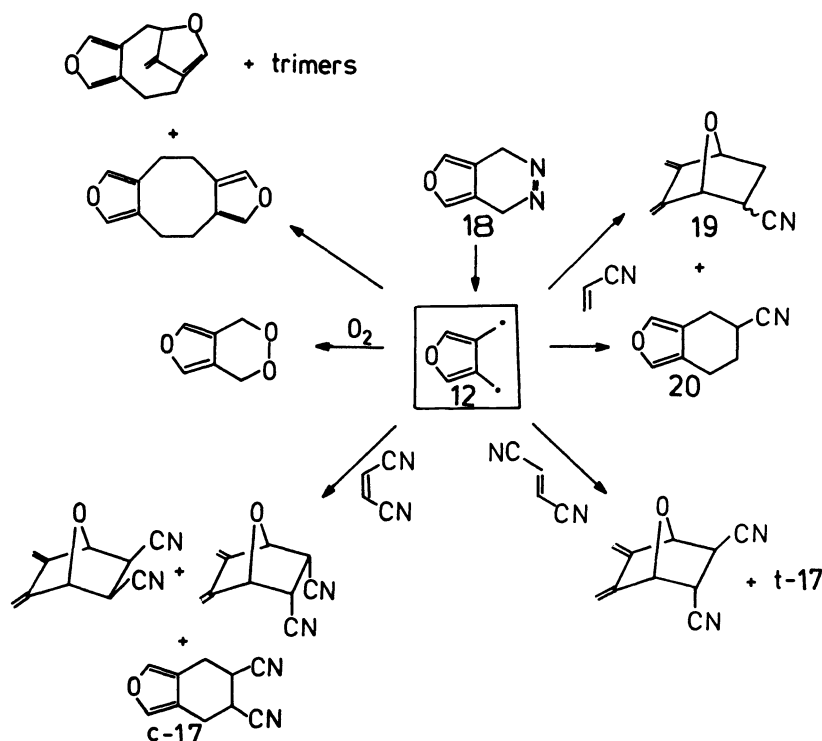
[b] STO-3G/3-21G SDTQ CI, at 3-21G UHF triplet geometry, ref. 33.

[c] SVP SDTQ CI, ref. 34.

These biradicals have been invoked as reactive intermediates in the chemistry of the corres-
ponding diallenyl systems 14 and 15 (refs. 35 - 37), and 14 is thought to be formed in the
pyrolysis of 2,3-dimethylene-7-oxabicyclo[2.2.1]heptane (16) (ref. 38). Recent work (ref.
39) reports new methods for the generation of biradicals 12 and 13 from the corresponding
diazenes under circumstances that permit studies of their spectroscopic and chemical proper-
ties. Some of the observed transformations in the oxygen series are outlined in Scheme 1.

14: X=O   16
15: X=S

Scheme 1

The trapping reactions shown proceed in high yield. The ratio of products from acrylonitrile, endo-19:exo-19:20 = 64:24:12 is independent of the concentration of acrylonitrile in the range of 0.003 - 14M and also independent of the concentration of O_2.

Photolysis of the diazene 18 in glassy media at 77K generates an intense purple color associated with the biradical 12. The UV-Vis absorption spectrum shows three new maxima at 338, 348, and 560 nm ($\epsilon > 10^3$). These bands disappear when the matrix is melted, but in an appropriately high-melting medium, e.g. polycrystalline toluene, the color persists up to at least 160K. Similar phenomena are observed in the sulfur case 13. The oxygen transient 12 has been observed by picosecond flash photolysis and its reaction with O_2 monitored by that technique. In a system purged with N_2, the apparent lifetime of 12 is 3-4 µs.

Irradiation of the diazene 18 or its thiophene counterpart (18, S instead of O) in a 2-methyltetrahydrofuran glass at 12-80K in the microwave cavity of an EPR spectrometer generates the intense purple color but does not give rise to a detectable triplet signal.

Although assignments of the lowest energy spin states of 12 and 13 are still tentative, all of the evidence to date is consistent with a singlet in each case. The apparent experimental confirmation of the predicted violation of Hund's rule supports the practical value of both semi-empirical INDO/S-CI and ab initio quantum mechanical calculations in guiding the search for non-Kekulé molecules with low-spin ground states.

REFERENCES

1. For the coinage of the word "non-Kekulé", see M.J.S. Dewar, "Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969, p. 233.
2. M. Rule, A.R. Matlin, D.E. Seeger, E.F. Hilinski, D.A. Dougherty and J.A. Berson, Tetrahedron, 38, 787 (1982).

3. F. Hund, Z. für Physik, 51, 759 (1928).
4. R.S. Mulliken, Phys. Rev., 31, 587 (1928).
5. J.E. Lennard-Jones, Trans. Faraday Soc., 25, 668 (1929).
6. C. Coulson, "Valence", Oxford University Press, New York, 1952, p. 99.
7. H.C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).
8. L. Salem and C. Rowland, Angew. Chem. Intl. Ed. Engl., 11, 92 (1972).
9. For further discussion, see (a) J.P. Colpa, Molec. Phys., 28, 581 (1974);(b) J.P. Colpa,
    A.J. Thakkar, V.J. Smith, Jr. and P. Randle, ibid., 29, 1861 (1975); (c) J.M. McBride
    and M.W. Vary, Tetrahedron, 38, 765 (1982); (d) J.A. Berson, in "Quinones", vol. II of
    "The Chemistry of Functional Groups", S. Patai and Z. Rappoport, eds., Wiley, New York,
    in press.
10. E. Hückel, Z. phys. Chem., Abt. B, 34, 339 (1936).
11. W. Schlenk and M. Brauns, Chem. Ber., 48, 661 (1915).
12. W. Schlenk and M. Brauns, Chem. Ber., 48, 716 (1915).
13. Ref. 1, p. 194.
14. H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950).
15. W. T. Borden and E. Davidson, J. Am. Chem. Soc., 99, 4587 (1977).
16. I. A. Misurkin and A. A. Ovchinnikov, Russ. Chem. Rev. (Engl. translation), 46, 967
    (1977).
17. A. A. Ovchinnikov, Theor. Chim. Acta, 47, 297 (1978).
18. H. Kollmar and V. Staemmler, Theor. Chim. Acta, 48, 223 (1978).
19. W. T. Borden, E. R. Davidson and P. Hart, J. Am. Chem. Soc., 100, 388 (1978).
20. P. M. Lahti, A. R. Rossi and J. A. Berson, J. Am. Chem. Soc., 107, 2273 (1985).
21. P. Dowd, J. Am. Chem. Soc., 92, 1066 (1970).
22. (a) D.A. Dixon, R. Foster, T. Halgren and W.N. Lipscomb, J. Am. Chem. Soc., 100, 1359
    (1978).(b) For a review, see J.J. Gajewski, "Hydrocarbon Thermal Isomerizations",
    Academic Press, New York, 1981, pp. 138-155.
23. R. Schmidt and H.-D. Brauer, Angew. Chem. Intl. Ed. Engl., 10, 506 (1971).
24. W.R. Roth and G. Erker, Angew. Chem. Intl. Ed. Engl., 12, 503 (1973).
25. W. Grimme and H.J. Rother, Angew. Chem. Intl. Ed. Engl., 12, 502 (1973).
26. N.L. Bauld and C.-S. Chang, J. Am. Chem. Soc., 94, 7594 (1972).
27. W.R. Roth and B.P. Scholz, Chem. Ber., 115, 1197 (1982).
28. D.E. Seeger and J.A. Berson, J. Am. Chem. Soc., 105, 5144 (1983).
29. D.E. Seeger and J.A. Berson, J. Am. Chem. Soc., 105, 5146 (1983).
30. D.E. Seeger, P.M. Lahti, A.R. Rossi and J.A. Berson, J. Am. Chem. Soc., 108, 1251 (1986).
31. D.E. Seeger, E.F. Hilinski and J.A. Berson, J. Am. Chem. Soc., 103, 720 (1981).
32. (a) J. Ridley and M. Zerner, Theor. Chim. Acta, 32, 11 (1973); (b) ibid., 42, 233 (1976).
33. P.M. Lahti, Ph.D. Thesis, Yale University, 1985.
34. P. Du, D.A. Hrovat and W.T. Borden, J. Am. Chem. Soc., submitted.
35. (a) P.J. Garratt and S.B. Neoh, J. Am. Chem. Soc., 97, 3255 (1975); (b) P.J. Garratt
    and S.B. Neoh, J. Org. Chem., 44, 2667 (1979).
36. S. Braverman, U. Duar and D. Segev, Tetrahedron Lett., 3181 (1976).
37. Y.S.P. Cheng, E. Dominguez, P.J. Garratt and S.B. Neoh, Tetrahedron Lett., 6914 (1978).
38. P. Vogel and M. Hardy, Helv. Chim. Acta, 57, 196 (1974).
39. K.J. Stone, M.M. Greenberg, J.L. Goodman, K.S. Peters and J.A. Berson, J. Am. Chem. Soc.
    submitted.