

Violations of Hund's Rule in Non-Kekulé Hydrocarbons: Theoretical Prediction and Experimental Verification

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Non-Kekulé molecules are molecules that are fully conjugated but each of whose Kekulé structures contains at least two atoms that are not π -bonded.¹ Some examples of such hydrocarbons are trimethylenemethane (TMM), *m*-benzoquinodimethane (MBQDM), tetramethylethane (TME), and 1,2,4,5-tetramethylenbenzene (TMB). These four non-Kekulé hydrocarbons are depicted in Figure 1.

In 1950 Longuet-Higgins proved that, in a non-Kekulé hydrocarbon that contains no $4n$ -membered rings, the number of atoms that cannot be assigned to π bonds is equal both to the number of π nonbonding molecular orbitals (NBMOs) and to the number of electrons that must be accommodated in them.¹ Thus, each of the molecules in Figure 1 has two π NBMOs, which contain a total of two electrons. Hence, as implied by the Kekulé structures in Figure 1, each of these molecules is a diradical.

On the basis of Hund's rule,² Longuet-Higgins predicted that the ground state of a non-Kekulé hydrocarbon with n electrons in n π NBMOs would have a spin quantum number of $S = n/2$.¹ Were this prediction correct, each of the diradicals in Figure 1 should have a triplet ground state ($S = 1$), in which the two nonbonding electrons occupy different NBMOs and have parallel spins. Therefore, each of these diradicals should be paramagnetic. The finding that the ground state of one or more of these molecules was calculated to be a singlet and/or was determined experimentally to be diamagnetic would constitute a violation of Hund's rule, at least as applied to non-Kekulé hydrocarbons by Longuet-Higgins.

Weston Thatcher Borden received his undergraduate degree from Harvard in 1964. Following a year spent on a Fulbright Fellowship studying theoretical chemistry with H. C. Longuet-Higgins, he returned to Harvard and, under the guidance of E. J. Corey, was awarded a Ph.D. in 1968. After another five years on the faculty of the same institution, he joined the Chemistry Department at the University of Washington. His research activities include the synthesis and study of molecules of theoretical interest and the application of qualitative molecular orbital theory and quantitative *ab initio* calculations to the understanding of organic chemistry.

Hiizu Iwamura was born in Tokyo and raised in Miyazaki, Japan. He received his B.Sc., M.Sc., and Ph.D. (1982) degrees from the University of Tokyo. He was appointed Assistant Professor and in 1970 Associate Professor at the University of Tokyo. In 1977 he joined the Institute for Molecular Science in Okazaki as Professor and Head of the Division of Applied Molecular Science. He returned to his *alma mater* in 1987 as Professor of Chemistry. His research work in physical organic chemistry has focused on the design, synthesis, and analysis of compounds of theoretical interest.

Jerome A. Berson was born in Sanford, FL, in 1924. He received his degrees from the City College of New York (B.S.) and Columbia University (M.A. and Ph.D. with W. von E. Doering), and he did postdoctoral research at Harvard University (with R. B. Woodward). An academic since 1950, he taught successively at the University of Southern California and the University of Wisconsin and is now Sterling Professor of Chemistry at Yale University. He and his collaborators focus their research on the mechanisms of organic reactions and the synthesis of molecules designed to test theoretical concepts.

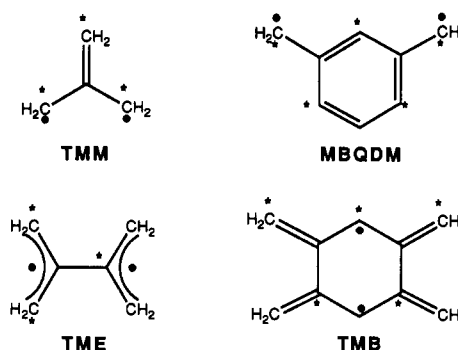


Figure 1. Some non-Kekulé hydrocarbon diradicals. Starred and unstarred carbons¹ are shown.

This Account provides a brief history of the search for violations of Hund's rule in non-Kekulé molecules. It describes why such violations were predicted and how they were subsequently confirmed experimentally, first in dicarbenes, subsequently in dinitrenes and dinitroxides, and finally in a non-Kekulé hydrocarbon.

An Unsuccessful Experiment Leads to a Theory

In 1968 W.T.B. joined Paul Dowd on the faculty at Harvard. Dowd had already succeeded in generating TMM and recording its triplet EPR spectrum,^{3a} and he was well on the way to doing the same for TME.^{4a} W.T.B. suggested to Dowd that they collaborate on obtaining the EPR spectrum of triplet 1,3,5,7-cyclooctatetraene (COT).

The plan was to incorporate COT and a triplet sensitizer into an organic glass at low temperature, irradiate the glass, and detect the triplet COT formed by energy transfer from the sensitizer. Unfortunately, when the experiment was performed, no trace of a triplet EPR signal from COT was observed.

The success of this experiment was predicated on the assumption that triplet COT at its octagonal equilibrium geometry would lie below the lowest singlet state in energy. This seemed to be a safe assumption,

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(1) Longuet-Higgins, H. C. *J. Chem. Phys.* 1950, 18, 265.

(2) Hund, F. *Linienpektren Periodisches System der Elemente*; Springer-Verlag: Berlin, 1927, p 124 ff; Hund, F. *Z. Phys.* 1928, 51, 759.

(3) (a) Dowd, P. *J. Am. Chem. Soc.* 1966, 88, 2587. (b) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* 1976, 98, 5726.

(c) Review: Berson, J. A. In *Diradicals*, Borden, W. T. Ed.; Wiley-Interscience: New York, 1982; pp 151–194.

(4) (a) Dowd, P. *J. Am. Chem. Soc.* 1970, 92, 1066. (b) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* 1986, 108, 7416.

since in planar COT two electrons must be placed in a pair of degenerate NBMOs. Therefore, Hund's rule predicts that the triplet should be the lowest energy state. Moreover, experiments by Wasserman and co-workers on pentachlorocyclopentadienyl cation,⁵ another annulene with $4n$ π electrons, had shown it to have a triplet ground state.⁶ However, when all attempts to detect triplet COT failed, it seemed worth testing computationally the assumption that the triplet at its D_{8h} equilibrium geometry was, indeed, the state of lowest energy.

Back-of-the-envelope calculations on $[4n\pm 1]$ - and $[4n\pm 2]$ annulenes with $4n$ π electrons found the triplet to be the lowest energy state at the geometry of highest symmetry.⁷ However, the same calculations on $[4n]$ -annulenes, such as cyclobutadiene (CBD) and COT, found the singlet and triplet to have nearly the same energy. In fact, when correlation is included between the electrons in the NBMOs and those in the bonding π MOs, the singlet is actually computed to be well below the triplet in energy, both in square CBD⁸ and in octagonal COT.⁹

A very simple explanation was provided for the predicted violation of Hund's rule in square CBD.¹⁰ The physical basis for Hund's rule is that, when two electrons have the same spin, the Pauli exclusion principle¹¹ does not allow the electrons simultaneously to occupy the same region of space. Since electrons of opposite spin are not prevented by the Pauli principle from appearing in the same region of space, they usually have a much higher mutual Coulombic repulsion energy than two electrons of the same spin.

However, as shown in Figure 2, the degenerate Hückel NBMOs for square CBD can be chosen so that they are *disjoint*, i.e., have no atoms in common. In both the lowest singlet and the lowest triplet state of square CBD one electron occupies each of these NBMOs.¹² Because these MOs are disjoint, regardless of whether the electrons in them have the same or opposite spin, there is no probability that both electrons will simultaneously occupy the same AO. Thus, to a first approximation, the lowest singlet and the lowest triplet state of square CBD have the same energy.

(5) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

(6) (a) Subsequent experiments showed the parent cyclopentadienyl cation also to have a triplet ground state: Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffmann, J. M.; Perchonok, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 13017. (b) Hexachlorobenzene dication was later found to have a triplet ground state, too: Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965. (c) Review: Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27.

(7) Borden, W. T. *J. Chem. Soc., Chem. Commun.* **1969**, 1968.

(8) Craig, D. P. *Proc. R. Soc. London, A* **1950**, *202*, 498. Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354. Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583. Borden, W. T.; Davidson, E. R.; Hart, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 388. Jafri, J. A.; Newton, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5012. Agren, H.; Correia, N.; Flores-Riveros, A.; Jensen, H. J. A. *Int. J. Quantum Chem.* **1986**, *19*, 237. Nakamura, K.; Osamura, Y.; Iwata, S. *Chem. Phys.* **1989**, *135*, 67.

(9) (a) Dewar, M. J. S.; Merz, K. M. *J. Phys. Chem.* **1985**, *89*, 4739. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(10) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968.

(11) The Pauli principle is embodied in the antisymmetrization of electronic wave functions.

(12) In terms of the NBMOs shown in Figure 2, the lowest energy singlet wave function takes the form $|\psi_x\psi_y(\alpha\beta - \beta\alpha)/(2)^{1/2}\rangle$. If MOs, ψ_x and ψ_y , that are the sum and difference of those in Figure 2 are used, the same wave function takes a different form and requires two configurations, $|\psi_x^2\rangle - |\psi_y^2\rangle$. When ψ_x and ψ_y are not exactly degenerate, the weights of these two configurations are not exactly equal.

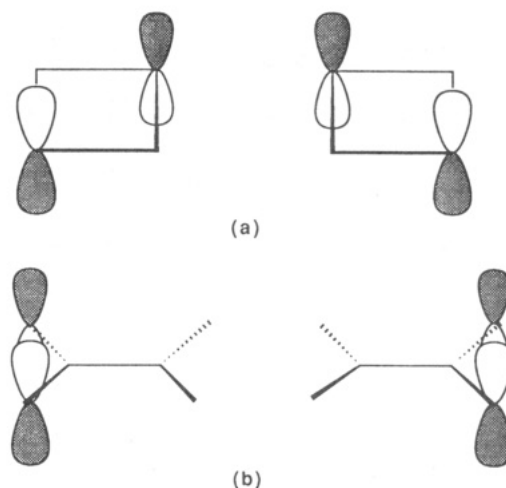


Figure 2. Disjoint NBMOs for (a) CBD and (b) TME.

Moreover, since in the lowest singlet the two electrons in the NBMOs have opposite spin, it is possible for each of the electrons in the bonding π MO to localize partially at the same pair of carbons as the nonbonding electron that has the same spin.¹⁰ This type of correlation between the electrons in the bonding and nonbonding MOs is energetically advantageous, because electrons of the same spin cannot appear simultaneously in the same AO. However, this type of electron correlation is not possible in the triplet state, because the two electrons in the NBMOs have the same spin. Consequently, including correlation between the bonding and nonbonding π electrons drops the energy of the singlet well below that of the triplet in square CBD.¹³

When the Hückel NBMOs of a diradical are *non-disjoint*, a triplet ground state is expected,¹⁴ because in this state the Pauli principle prevents the two electrons in the NBMOs from simultaneously appearing in the AOs that the two NBMOs have in common.¹⁵ The degenerate MOs of $[4n\pm 1]$ - and $[4n\pm 2]$ annulenes are nondisjoint, as are the NBMOs of many non-Kekulé hydrocarbons. As expected from the fact that diradicals such as cyclopentadienyl cation, TMM, and MBQDM have nondisjoint NBMOs, they have all been calculated¹⁷ and found¹⁸ to have triplet ground states, as predicted by Hund's rule.

(13) This effect has been given the name "dynamic spin polarization", and it has been shown to be responsible for the violation of Hund's rule that is predicted for twisted (D_{2d}) ethylene: Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223.

(14) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Review: Borden, W. T. In *Diradicals*, Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1-72.

(15) In nondisjoint diradicals the NBMOs for the lowest singlet state differ from those for the triplet, since the NBMOs for the singlet tend to localize the electrons of opposite spin to different regions of space. This localization in nondisjoint, singlet diradicals is responsible for phenomena as diverse as the difference between the geometries of singlet and triplet TMM,^{16a-d} the ability of heteroatom substitution selectively to stabilize singlet states,^{16e-h} and the dramatic reduction in the singlet-triplet splitting on replacing the hydrogen in nitrene (NH) with a phenyl substituent.¹⁶ⁱ

(16) (a) Borden, W. T.; Salem, L. *J. Am. Chem. Soc.* **1973**, *95*, 932. (b) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 2907. (c) Borden, W. T. *J. Am. Chem. Soc.* **1976**, *98*, 2695. (d) Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* **1976**, *64*, 663. (e) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112. (f) Coolidge, M. B.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751. (g) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 3773. (h) Fort, R. C., Jr.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549. (i) Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8698.

Predicted Violations of Hund's Rule in Non-Kekulé Hydrocarbons

Since a square geometry for CBD and an octagonal geometry for COT are the transition states for bond shifting in the lowest singlet state of both these $[4n]$ -annulenes,^{8,9b} it is difficult to provide unequivocal experimental proof that at these geometries the triplet does not fall below the singlet in energy. Proof of a violation of Hund's rule should, at least in principle, be easier to obtain at the equilibrium geometry of a non-Kekulé hydrocarbon than at the transition state for bond shifting in a $[4n]$ annulene.

Violations of Hund's rule in non-Kekulé hydrocarbons are predicted to be most likely to occur in those that have disjoint NBMOs.¹⁴ Determining whether a non-Kekulé hydrocarbon has disjoint Hückel NBMOs can be readily accomplished, either by using the zero-sum rule to find the NBMOs¹ or simply by counting to determine whether the numbers of starred and unstarred atoms are the same. If $N^* = N$, one NBMO is confined to the starred set of atoms, the other to the unstarred set.^{14,19} The latter method quickly establishes that, of the diradicals shown in Figure 1, TME and TMB are disjoint and thus are promising candidates to violate Hund's rule.

TME. *Ab initio* calculations on TME at many different levels of theory all predict a singlet ground state for the planar diradical.^{14,20} The predicted violation of Hund's rule at this geometry is a consequence of two effects. One is long-range bonding between the termini of the two allylic radicals in the singlet. Its magnitude can be assessed from calculations that utilize two configurations for the singlet (TCSCF)¹² and one for the triplet (ROHF). At this level the singlet is calculated to lie below the triplet by about 1.8 kcal/mol with Dunning's SVP basis set.^{20a,b}

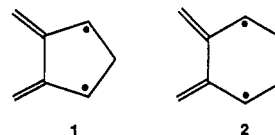
The second effect that stabilizes the singlet, relative to the triplet, is interaction between the negative spin densities in the $p-\pi$ AOs at the central carbons of the two allylic radicals in TME.¹⁴ This interaction, like that between the electrons at the terminal carbons, is bonding in the singlet. Since negative spin density appears only in calculations in which correlation is provided between the electrons within each allylic radical, the size of this second effect can be assessed by comparing the results of CASSCF calculations, which correlate all six π electrons in TME, with the TCSCF/ROHF results. At the CASSCF level the singlet is calculated to lie 3.8 kcal/mol below the triplet,^{20b} an energy difference that is more than twice as large as that computed at the TCSCF/ROHF level.

Confirming experimentally the predicted violation of Hund's rule in planar TME is very difficult, since the equilibrium geometry of neither the singlet nor the

triplet is expected to be planar.^{20,21} At the nonplanar equilibrium geometry of the triplet state, SD-CI calculations that correlate all the valence electrons find that, after a correction for the effect of quadruple excitations, the triplet is actually calculated to lie slightly below the singlet in energy.^{20c,22}

A triplet that is metastable at its equilibrium geometry provides an explanation for Dowd's findings that TME has a triplet EPR spectrum^{4a} and that a plot of the intensity of the spectrum versus $1/T$ is linear.^{4b} The linear Curie plot indicates that either the triplet state is lower in energy by several hundred calories/mole than any singlet state with which it is in equilibrium or two states have the same energy to within about 10 cal/mol.

Roth and co-workers have also found a triplet EPR spectrum and a linear Curie plot for the 2,2-dimethyl derivative of 1,²³ a TME in which planarity is enforced by incorporation of two termini into a five-membered ring. This finding might seem to disprove the prediction that planar TME should violate Hund's rule. However, the hyperconjugative interaction between the bonds to the additional carbon in 1 and the adjacent radical centers is calculated at the SD-CI level of theory to make the triplet the ground state.^{24,25} A triplet is both calculated²⁷ and found²⁸ to be the ground state of the closely related diradical, cyclopentane-1,3-diyl.



Were TME derivative 2 planar, it would be a better candidate than 1 for having a singlet ground state. However, the equilibrium geometry of 2 is computed to be nonplanar, and at the SD-CI level this leads to a very small calculated preference for a triplet ground state.²⁴ This computational finding is consistent with the experimental results of Dowd and co-workers for 2.²⁹

Several derivatives of 1 with a heteroatom (e.g., N, O, or S) in place of the central CH_2 group have been

(21) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. M. *J. Am. Chem. Soc.* 1978, 100, 1359.

(22) These CI calculations^{20c} were much larger than the previous CASSCF calculations,^{20b} which found the singlet to lie below the triplet at all geometries. However, the CI calculations were based on TCSCF and ROHF reference wave functions, rather than on CASSCF reference wave functions that correlate all six π electrons. Consequently, the CI calculations are likely to underestimate π correlation effects, which selectively stabilize the singlet, even at the triplet D_2 equilibrium geometry. In fact, with CASSCF reference wave functions, CASPT2N calculations, which use second-order perturbation theory, instead of CI, for calculating the rest of the electron correlation energy, give almost exactly the same singlet-triplet energy differences as the CASSCF calculations (Hrovat, D. A.; Borden, W. T. Unpublished results).

(23) Roth, W. R.; Kowalczyk, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Muller, P. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1285.

(24) Nash, J. J.; Dowd, P.; Jordan, K. D. *J. Am. Chem. Soc.* 1992, 114, 10071.

(25) However, calculations which correlate just the π electrons find a singlet ground state and a very low-lying triplet state for 1.²⁶

(26) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* 1986, 108, 8086.

(27) Conrad, M.; Pitzer, R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1979, 101, 2245. Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F., III. *J. Phys. Chem.* 1992, 96, 3712.

(28) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* 1975, 97, 3857. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* 1979, 101, 4688.

(29) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* 1987, 109, 5284.

(17) (a) CPD⁺: Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1979, 101, 3771. (b) TMM: See refs 16a-d and the following: Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1979, 101, 8009. Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1982, 104, 967. (c) MBQDM: See ref 16h and the following: Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1983, 105, 1791.

(18) (a) CPD⁺: See ref 6a. (b) TMM: See ref 3b. (c) MBQDM: Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* 1983, 105, 628.

(19) If $N^* \neq N$, then $N^* - N$ NBMOs are confined to the starred set of atoms. However, the NBMOs may still be disjoint.¹⁴

(20) (a) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* 1987, 109, 930. (b) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* 1992, 114, 4743. (c) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* 1993, 115, 270.

calculated^{24,26} and/or found³⁰ to be ground-state singlets. However, the π lone pair of the heteroatom strongly lifts the approximate degeneracy between the NBMOs that exists in planar TME. Therefore, the singlet ground states found for these heteroatom derivatives of 1³⁰ do not provide confirmatory evidence for the prediction of a singlet ground state for planar TME.

TMB. Given the problems in devising an electronically unperturbed derivative of TME that is restricted to a planar geometry, TMB would appear to be a better candidate for a diradical in which a violation of Hund's rule might be found experimentally. The two pentadienyl radical moieties in TMB are constrained to be coplanar by the two C-C bonds that join them. Therefore, unlike the case in TME, a planar geometry for TMB seems assured.

Both semiempirical and *ab initio* calculations predict a singlet ground state for TMB.³¹ With Dunning's SV basis set the singlet is calculated to lie below the triplet by 1.8 kcal/mol at the TCSCF/ROHF level and by 5.0–6.6 kcal/mol when correlation is provided for all the π electrons.^{31d} With the 6-31G* basis set the TCSCF/ROHF energy difference is essentially unchanged from the SV value, and CASSCF/6-31G* calculations that correlate all 10 π electrons find a singlet-triplet splitting of 4.8 kcal/mol.^{31e} The much larger singlet-triplet energy differences that are calculated with both basis sets when all the π electrons are correlated indicate that the negative spin densities at the carbons where the pentadienyl radicals are joined play a major role in making the singlet the predicted ground state of TMB.^{31d} Experiments, performed in order to test the prediction that a violation of Hund's rule should be found in TMB, are described in the final section of this Account.

Predictions Made using Valence Bond (VB) Theory. The qualitative predictions of violations of Hund's rule in TME and TMB can also be made using VB rather than MO theory. The MO approach starts with the Hückel orbitals, which maximize bonding. As described above, classifying the Hückel NBMOs as disjoint or nondisjoint allows the determination of how the spin state affects the Coulombic repulsion between the electrons in these orbitals.¹⁴ In contrast, VB theory starts by assigning one electron to each AO, thus minimizing electron repulsion. The lowest energy spin state is then the one that maximizes bonding between electrons in AOs on adjacent atoms.³²

Using the VB approach, Ovchinnikov derived the formula $S = (N^* - N)/2$,³³ which also predicts a singlet, $S = 0$, ground state for TME and TMB. Klein and co-workers have provided a more rigorous derivation

(30) (a) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088. (b) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567. (c) Zilm, K. W.; Merrill, R. A.; Webb, G. G.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1533. (d) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A.; Merrill, R. A.; Duchamp, J. C.; Zilm, C. *J. Am. Chem. Soc.* **1991**, *113*, 2318.

(31) (a) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2318. (b) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958. (c) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4362. (d) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072. (e) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, submitted.

(32) For a review that compares the MO and VB approaches for making predictions of the spins of ground states, see: Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.

(33) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

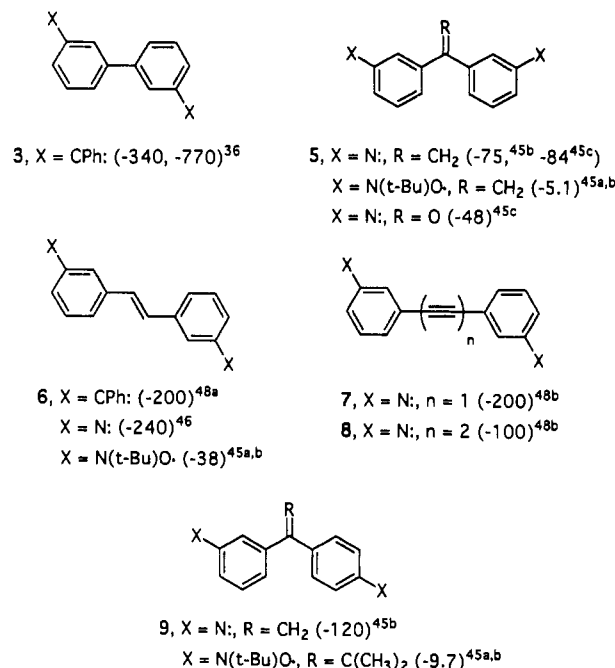


Figure 3. Disjoint hydrocarbons and heteroatom-perturbed analogs. The observed energy gaps, ΔE_{S-Q} for the dicarbenes and dinitrenes and ΔE_{S-T} for the dinitroxides, are given in parentheses in calories/mole. The negative signs indicate singlet ground states.

of this formula,³⁴ and they have also shown that it can be used to predict the ground states of conjugated polycarbenes, provided that each carbenic center is given a value of 2 in summing up the numbers of starred and unstarred atoms.³⁵

Violations of Hund's Rule in Conjugated Dicarbenes and Dinitrenes

The first violation of Hund's rule was detected by Itoh in 1978 in dicarbene 3, X = :CPh (Figure 3),³⁶ which is closely related to the Schlenk-Brauns non-Kekulé diradical 3, X = ·CPh₂.³⁷ Since $N^* = N$ in 3, the π NBMOs are disjoint. Hence, either from this perspective or from the application of Ovchinnikov's formula, a singlet ground state is predicted for planar 3.

Interestingly, in 1936, more than 40 years before Itoh's experiment on 3, X = :CPh, Hückel had pointed out that the lowest singlet and triplet state of 3, X = ·CPh₂, should be nearly degenerate, since one NBMO can be localized to just the starred carbons on the left-hand side of the diradical and the other NBMO can be localized to just the unstarred carbons on the right.³⁸ CI calculations by Baudet on the planar, non-Kekulé hydrocarbon, consisting of the central 14-carbon fragment of diradical 3, predicted the singlet to be the ground state, although by less than 1 kcal/mol.³⁹ Since, as in the case of TME, neither the lowest singlet nor the triplet state of 3 is likely to have a planar equilibrium

(34) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101.

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(36) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. Teki, Y.; Takui, T.; Kitano, M.; Itoh, K. *Chem. Phys. Lett.* **1987**, *142*, 181.

(37) Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 716.

(38) Hückel, E. *Z. Phys. Chem. (B)* **1936**, *34*, 339. We thank Dr. E. F. Hilinski for first bringing this paper to our attention.

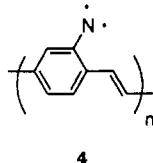
(39) Baudet, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 191.

geometry, the actual singlet–triplet energy separation in **3** is likely to be even smaller.

Indeed, Itoh established a singlet ground state for **3**, $X = \text{:CPh}$, by showing that the triplet and quintet states, which he detected by EPR, were very low-lying excited states that were thermally populated.³⁶ More recently, however, Lahti and co-workers were unable to detect EPR signals due to a quintet state of dinitrene **3**, $X = \text{N}$ ·, which was therefore concluded either to have a singlet ground state or, probably less likely, to behave like a pair of noninteracting triplet nitrenes.⁴⁰

A very recent experimental investigation by Rajca and co-workers also found very small singlet–triplet splittings in two sterically shielded derivatives of the Schlenk–Brauns diradical, but the triplet was found to be the ground state in both.⁴¹ The ortho substituents in these derivatives of **3**, $X = \text{:CPh}_2$, undoubtedly cause their geometries to differ from that of the unsubstituted diradical. Therefore, it still remains possible that a reinvestigation of the magnetic properties of **3**, $X = \text{:CPh}_2$,⁴² would reveal that the first non-Kekulé hydrocarbon to violate Hund's rule was actually prepared by Schlenk and Brauns in 1915.³⁷

A series of non-Kekulé dicarbenes and dinitrenes carrying one or two benzene rings has been prepared and studied in the labs of H.I. at the University of Tokyo as prototypes for the dimer units of super-high-spin polycarbenes and polynitrenes, e.g., **4**.⁴³ All of the



4

nondisjoint dicarbenes and dinitrenes that were prepared were found experimentally to have quintet ground states, thereby establishing the potential usefulness of these dimer units for the construction of magnetic materials.⁴⁴ Since the corresponding singlet states could not be populated thermally in the limited temperature range accessible for the study of these reactive species, only lower limits of several hundred calories/mole for the energy gaps, ΔE_{S-Q} , between the quintet and singlet states could be established.

It having been shown that a variety of nondisjoint dicarbenes and dinitrenes have high-spin ground states, a systematic experimental study was begun of the predicted violations of Hund's rule in disjoint systems.⁴⁴ All of the dicarbenes and dinitrenes in Figure 3 are disjoint; and all were, in fact, found experimentally to have singlet ground states. Since in most cases the quintet excited states are close enough to the singlet ground states to be populated thermally, the ΔE_{S-Q} values have been determined and are given in Figure 3.

(40) Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532.

(41) Rajca, A.; Utamapanya, S.; Smithhisler, D. J. *J. Org. Chem.* **1993**, *58*, 5650.

(42) Müller, E.; Müller-Rudloff, I. *Justus Liebigs Ann. Chem.* **1936**, *517*, 134.

(43) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1991**, *24*, 1077.

(44) Iwamura, H. *Pure Appl. Chem.* **1993**, *65*, 57. Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 233.

Some of the molecules in Figure 3, e.g., **3**,^{36,40} and **9**,⁴⁵ have disjoint Hückel π NBMOs which, like those in TME, are separated by two carbons at which both NBMOs have nodes. In **6**,^{46,47} and **7**,⁴⁸ the Hückel π NBMOs are separated by four such carbon atoms, and in **8** the Hückel π NBMOs are separated by six nodal carbons. It can be seen in the structurally related series **3**, **6**, **7**, **8** that, as the numbers of nodal carbon atoms separating the two localized NBMOs increase, the energy gaps between the singlet ground states and the quintet excited states become smaller.

In **5** the disjoint Hückel π NBMOs are separated by three nodal carbon atoms. The NBMOs in **5** are thus related in connectivity to those in pentamethylenepropane (PMP), another disjoint, non-Kekulé, hydrocarbon diradical.¹⁴ From MO theory one might expect **5** to have a singlet ground state and a smaller energy separation between it and the lowest excited state than **9**, which is related to TME. In contrast, naive application of Ovchinnikov's formula predicts $S = 2$ for dinitrene **5**, $X = \text{N}$ ·, and $S = 1$ for the corresponding dinitroxide. Of course, the formula provides no information about the size of the energy gaps between the high-spin ground states and the lowest singlet excited states that it predicts for these molecules.³²

Recent studies of **5**, $X = \text{N}$ · and $X = \text{N}(t\text{-Bu})\text{O}^{\bullet}$ (see next section), constitute the first experimental investigations of disjoint systems of the PMP type.⁴⁵ Both **5**, $X = \text{N}$ ·, and **5**, $X = \text{N}(t\text{-Bu})\text{O}^{\bullet}$, were found to have a singlet ground state. Moreover, as expected, smaller values of ΔE_{S-Q} and ΔE_{S-T} were measured in, respectively, **5**, $X = \text{N}$ ·, and **5**, $X = \text{N}(t\text{-Bu})\text{O}^{\bullet}$, than in **9**, $X = \text{N}$ ·, and **9**, $X = \text{N}(t\text{-Bu})\text{O}^{\bullet}$.

Dinitroxide Analogs of Non-Kekulé Hydrocarbons

All of the non-Kekulé hydrocarbons discussed above and their dicarbene and dinitrene analogs are reactive intermediates that can be studied only under high dilution in inert solid solutions at cryogenic temperatures. The preparation of high-spin polyradicals that are persistent at ambient temperatures is highly desirable, since they are expected to show interesting magnetic properties and possibly to provide the basis for novel magnetic materials.

Toward this end, the group at the University of Tokyo has prepared a variety of analogs of non-Kekulé hydrocarbons in which the reactive benzylic radical sites are replaced with the considerably more stable *tert*-butyl nitroxide radicals.^{45a,b,49} The relative energies of the spin states of the dinitroxides are consistent with those found for the corresponding dicarbenes and dinitrenes. High-spin ground states are found for the dinitroxides when the corresponding non-Kekulé hydrocarbons are nondisjoint; and, again in violation of

(45) (a) Matsumoto, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 5448. (b) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952. (c) Ling, C.; Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1992**, *114*, 9959.

(46) Doi, T.; Koga, N.; Iwamura, H. Unpublished results.

(47) Weak antiferromagnetic coupling has been reported between the spins in the disjoint NBMOs of a perchlorinated tetraradical that is related to **6**: Carilla, J.; Juliá, L.; Riera, J.; Brillias, E.; Garrido, J. A.; Labarta, A.; Alcalá, R. *J. Am. Chem. Soc.* **1991**, *113*, 8281.

(48) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

(49) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346.

Hund's rule, singlet ground states are found for the dinitroxide analogs of disjoint non-Kekulé hydrocarbons.

As shown by the results for the disjoint molecules in Figure 3, the size of the energy gap between the ground state and the lowest energy excited state is in every case smaller in the dinitroxide than in the corresponding dicarbene or dinitrene. This is not surprising, since both calculations and experimental data indicate that delocalization of spin density into the benzene ring of a phenyl nitroxide is only about 50–70% of the delocalization of spin density into a benzene ring of triphenylmethyl radical or diphenylcarbene.

The attenuation of the size of the singlet–triplet energy gaps in dinitroxides bodes ill for the construction of magnetic materials, based on super-high-spin polynitroxides. Even when the ground state of a polynitroxide has high spin, lower spin states will be thermally populated at ambient temperatures. On the other hand, the attenuated interaction between the unpaired spins in dinitroxides has enabled the experimental determination of the size of the singlet–triplet energy gaps in some nondisjoint systems, where the energy differences between spin states are too large to be obtained from Curie plots of the EPR data for the corresponding non-Kekulé hydrocarbons, dicarbenes, or dinitrenes.^{44,45a,b,49}

As noted in the section on TME, the finding that a Curie plot of the intensity of an EPR spectrum versus $1/T$ is linear has two possible interpretations. Either the high-spin state being observed is the ground state and is separated by at least several hundred calories/mole from excited states of lower spin multiplicity, or it is nearly degenerate with a state of lower spin. This ambiguity in interpretation is compounded by the experimental difficulties in performing reliable measurements of absolute EPR intensities in general and at temperatures lower than 10 K in particular.⁵⁰ Accurate measurements in this temperature range are required if the energy difference between the ground and lowest excited states is very small.

Measurements of paramagnetic susceptibility, χ , are often free from these difficulties.⁴⁹ Like the EPR signal intensities, the χ values for a single spin state are inversely proportional to temperature. The proportionality constant C is called the Curie constant and is given by the expression $C = Ng^2S(S + 1)\mu_B^2/3k$. A determination of χ at one temperature gives C at that temperature. The value of C can reveal whether a diradical under investigation is a pure triplet or a statistical 3:1 mixture of a triplet ($S = 1$) and a singlet ($S = 0$) state of equal energy, since $C = 1.0$ emu-K/mol for the former case and 0.75 emu-K/mol for the latter.

Measurement of the temperature dependence of C allows the determination of how the relative populations of high- and low-spin states depend on temperature. Energy differences between spin states of as little as a few calories/mole can be measured in this way. The energy gaps given for the disjoint dinitroxides in Figure 3 were all determined by measuring the temperature dependence of their paramagnetic susceptibilities.^{45a,b,49}

(50) Berson, J. A. In *The Chemistry of Quinonoid Compounds*; Patai, S. Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, pp 462–469.

TMB: A Non-Kekulé Hydrocarbon That Violates Hund's Rule

The foregoing sections have described violations of Hund's rule that have been found experimentally in dicarbenes, dinitrenes, and dinitroxides. Although these violations all occur in molecules with π systems that have disjoint NBOs, none of these molecules is, strictly speaking, a non-Kekulé hydrocarbon. In contrast, TMB is a non-Kekulé hydrocarbon and one for which both qualitative theory¹⁴ and quantitative calculations *unequivocally* predict a singlet ground state.³¹ It was particularly important, therefore, to establish experimentally whether the predicted violation of Hund's rule in TMB actually does occur.

The first published preparation of TMB^{51a} appeared in 1987. It described the generation of the TMB diradical by extrusion of carbon monoxide from 2,3,5,6-tetrakis(methylene)-7-norbornanone (10). Irradiation of this ketone in a rigid medium at low temperature produced a visibly colored preparation, with a UV–vis spectrum dominated by a strong band near 490 nm, which was flanked by several weaker bands. Infrared spectroscopy showed the characteristic carbon monoxide band at 2133 cm^{-1} , in addition to other new bands at 854 and 810 cm^{-1} , which were assigned⁵¹ to out-of-plane C–H bending vibrations in TMB.

Most strikingly, samples prepared by irradiation of ketone 10 in an adamantane matrix at 15 K displayed a strong electron spin resonance (EPR) spectrum, consisting of a narrow $\Delta m_s = 1$ transition (total width ~ 90 G) with discernible fine structure. The spectrum was interpreted with the zero-field splitting parameters $|D/hc| = 0.0042$ cm^{-1} and $|E/hc| = 0.0009$ cm^{-1} . A very weak resonance appeared at approximately half-field, which was assigned to the $\Delta m_s = 2$ transition. The intensity of the EPR signal obeyed the Curie law, which led the authors^{51a} to assign the ground state of TMB as a triplet. Further observations^{51a,b} were reported in support of this assignment. The authors⁵¹ concluded that the theoretical prediction of a singlet ground state for TMB was incorrect and that the hypothesis that violations of Hund's rule would be found in disjoint non-Kekulé hydrocarbons should be reexamined.

Work on TMB in the laboratories of J.A.B. at Yale had been under way since early 1986, when a small sample of ketone 10 from an independent synthesis, developed at the University of Lausanne by Rubello and Vogel and later published,⁵² became available. Subsequently, further quantities of 10 were prepared at Yale by both of the previous^{51,52} methods. The UV–vis, IR, and EPR spectroscopic studies at Yale on the transient purple species generated by irradiation of 10 matched those reported in 1987 by Roth and coworkers.^{51a}

The critical questions now were as follows: (1) Are the UV–vis and EPR spectra those of the same species? (2) Is either of the species TMB? (3) What is the spin

(51) (a) Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 256. (b) Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitz, A.; Lennartz, H.-W. *Chem. Ber.* 1991, 124, 2751.

(52) Rubello, A.; Vogel, P. *Helv. Chim. Acta* 1988, 71, 1268.

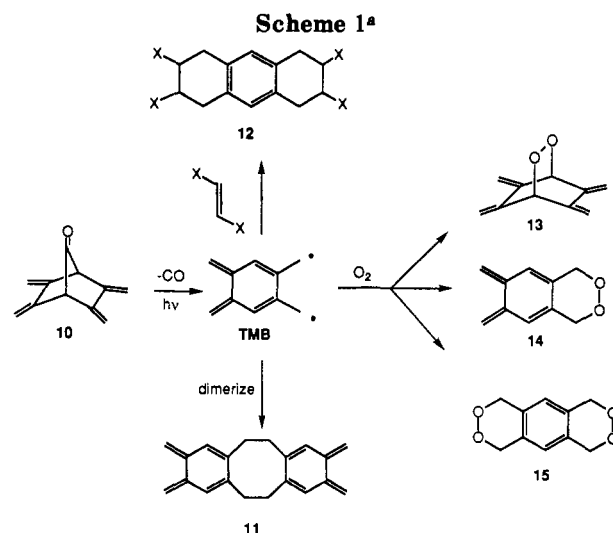
of the ground state of TMB? The answers eventually were found to be⁵³ (1) no; (2) yes; (3) singlet.

The published⁵¹ assignment of the EPR signal to TMB drew some skepticism, not only because of the conflict with theory but also because the zero-field splitting of the EPR signal of triplet TMB, as calculated by a calibrated point-dipole approximation method,⁵⁴ would be expected to be about 0.0165 cm⁻¹. This would have led to a separation between the outer wings of the spectrum that was about four times larger than the width of the EPR signal observed. Also, the intensity of the UV-vis absorption was not well correlated with the intensity of the EPR signal. These observations suggested the presence of an EPR-active species, *in addition to*, rather than identical with, the carrier of the purple transient, which was presumed to be TMB.

Further experiments by the Yale group⁵³ confirmed this view. Thus, an intensely purple glassy sample, prepared by 313-nm irradiation of ketone 10 in 2-methyltetrahydrofuran (MTHF) at 77 K, showed the characteristic UV-vis peak at 490 nm. When cooled to 10 K, this sample showed both the strong $\Delta m_s = 1$ EPR signal and the very weak $\Delta m_s = 2$ transition at 1650 G and 9.295 GHz. The sample was then photolyzed at 254 nm or with the unfiltered output of a 1000-W Hg-Xe lamp, both of which caused the disappearance of the purple color.⁵⁵ The UV-vis spectrum of the photobleached sample showed that >99% of the 490-nm absorption was gone, but the EPR spectrum of this same sample at 10 K revealed that the $\Delta m_s = 2$ transition was still present in undiminished intensity. In addition, the main ($\Delta m_s = 1$) transition was much stronger than before photobleaching, but its fine structure was lost. Thus, the intensity of the main transition apparently receives a significant contribution from one or more doublet species, which unavoidably biases the Curie law plot toward linearity.

These observations permit the conclusions that *at least two* EPR-active species are generated in these photolyses and that *none of the observed EPR signals are associated with the UV-vis spectrum*. Also, since no EPR signals are observed that have the zero-field splitting expected for TMB, it is unlikely that any appreciable quantity of authentic TMB triplet is present in the EPR preparations.⁵⁶ Therefore, at this stage, there was no longer any experimental basis for a challenge to the theoretical prediction of a singlet ground state for TMB. On the other hand, neither was there any conclusive proof that TMB violates Hund's rule by having a singlet ground state.

The Yale group⁵³ now adopted the working hypothesis that the EPR-silent purple UV-vis-active transient is



^a X = CO₂Et or CN.

in fact TMB and that its spin is singlet. The structural assignment is supported by several lines of evidence.

Scheme 1 shows the types of products that are observed when the TMB diradical is generated in fluid medium. The species can be intercepted in preparative experiments with alkenes to give adducts of the general structure 12 and with dioxygen to give the bridged mono- and diperoxides 13 and 15, respectively. Laser flash photolysis in fluid solutions with nanosecond time-resolved spectroscopy^{53b,c} gives direct evidence that the purple transient in the low-temperature matrix experiments is the reactive entity that produces these peroxides. The 490-nm absorption band of the diradical is quenched in a reaction that is first-order in O₂ with a rate constant of $1.85 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Some of this reaction leads to the very reactive fused peroxide 14, which can be recognized by its characteristic *o*-quinodimethane UV absorption maximum near 380 nm. Analysis of the growth and decay curves from laser flash experiments^{53c} shows that compound 14 is an intermediate in the formation of the fused diperoxide 15.

If the alkene trapping agents are not present in sufficient concentration to capture TMB, the diradical dimerizes to the double *o*-quinodimethane 11, which can be intercepted in yields of >70% in the form of a double Diels-Alder adduct. The reactive *o*-quinodimethane intermediate 11 again is recognized in laser flash experiments by the growth of the 380-nm chromophore at the same rate as the decay of the 490-nm absorption. These results provide confirmatory evidence that the carrier of the UV-vis spectrum, $\lambda_{\text{max}} = 490 \text{ nm}$, is not a minor species of undefined structure but rather is one that embodies the TMB unit.^{53c}

Although the absence of an observable EPR spectrum for TMB suggests that the substance is a singlet, this is essentially a negative experiment. NMR spectroscopy offers a more direct test. The uncompensated electron spins of a triplet species should give rise to severely contact-shifted, broadened lines, which normally would not be observed, whereas a singlet should give rise to unbroadened resonances in the usual chemical shift region.

A ¹³C-labeled sample of TMB was generated by photolysis of ketone 10, containing ¹³C in two adjacent

(53) (a) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* 1992, 114, 763. (b) Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Am. Chem. Soc.* 1992, 114, 5866. (c) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* 1993, 115, 8073.

(54) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* 1982, 38, 787 and references cited therein.

(55) Subsequent work showed that this photobleaching (which also had been observed by the Roth group) is associated with the successive cyclizations of the two exocyclic pairs of methylene groups of TMB, to give first [4,5]cyclobuta-*o*-quinodimethane and then benzof[1,2,4,5]-dicyclobutene.

(56) There remains the question of what species is the cause of the triplet EPR spectra. The narrow splitting would be consistent with the weak dipolar interaction of a radical pair, either intramolecular or intermolecular. For further discussion, see ref 53c.

CH₂ groups.^{53a,c} Application of techniques developed by Zilm^{30b-d} for low-temperature, solid-state, cross-polarization, magic-angle-spinning NMR spectroscopy revealed a single well-defined ¹³C resonance at 113 ppm. The growth in intensity of the new signal matched the loss in intensity of the precursor signal at 105 ppm; and the extent of conversion of the ketone to TMB, as measured by this NMR observation, matched that measured by UV-vis spectrometry at 490 nm. These observations show that the carrier of this NMR signal is TMB and that the spin state of TMB is singlet.

The TMB singlet is stable in rigid matrices at 77 K for weeks. Samples so treated still have the characteristic UV-vis spectrum and show no EPR spectrum. Although under these conditions the singlet state of TMB is *kinetically* stable with respect to conversion to the triplet, these experiments do not establish conclusively the *thermodynamic* stability of the former,

(57) Cases of slow interconversion of spin isomers of biradicals are known,⁶⁸ but the circumstances believed to be responsible for this phenomenon are not present in TMB.

(58) Bush, L. C.; Heath, R. B.; Berson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 9830.

relative to the latter. Nevertheless, it is unlikely that spin-state interconversion in TMB would be so slow that the singlet could be an excited state and not show any signs of decaying to the triplet ground state over a matter of weeks.⁵⁷ Therefore, the simplest interpretation of the kinetic stability of the singlet is that it is the ground state of TMB.⁵⁹ Thus, this disjoint diradical is the first non-Kekulé hydrocarbon for which there is strong experimental evidence for the violation of Hund's rule that is predicted theoretically.

We thank the coauthors whose names are given in the references for valuable insights and skilled experimental and computational contributions. This work was supported by the National Science Foundation of the United States, the Ministry of Education, Science and Culture of Japan, and the Nishida Research Fund for Fundamental Organic Chemistry.

(59) Note added in proof: Although π CI calculations on TMB^{31d} predict a UV-vis spectrum for the singlet which is quite different from that observed,^{51,53} calculations which include correlation between σ and π electrons predict a UV-vis spectrum for the singlet, but not the triplet, which is in excellent agreement with that observed.^{31e}