cess.[8] It is surprising to conclude that ISC of a relatively small diradical will be influenced by hyperfine coupling. It may be that the observed effect is, in fact, due to the hyperfine interaction in a small population of diradicals that have a structure for which electron exchange between the radical centers is very small. If this is true, then reduction of the exchange interaction might strongly enhance the magnitude of the observed effect.

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(4) Reviews: (a) Sagdaev, R. Z.; Salikhov, K. M.; Molin, Y. M. *Russ. Chem. Rev.* **1977**, *45*, 297. (b) Buchachenko, A. L. *Ibid.* **1976**, *45*, 375.
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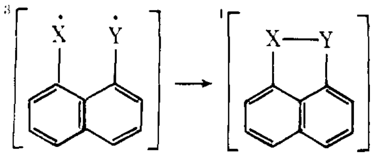
On the Mechanism of Intersystem Crossing and Ring Closure of the Triplet 1,8-Naphthoquinodimethane Biradical

Sir:

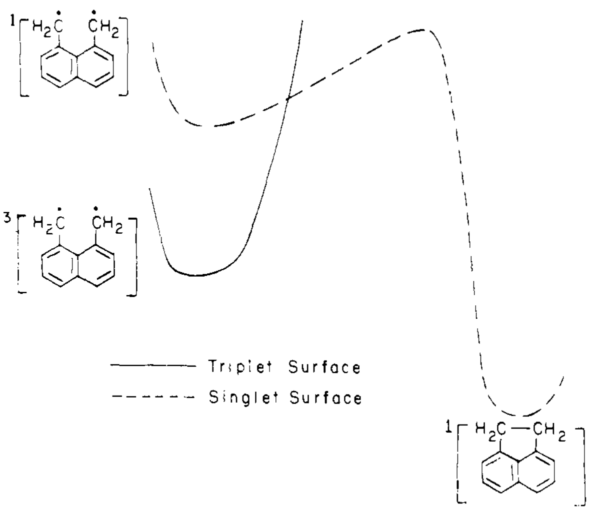
Triplet biradical intermediates are implicated in many photochemical[1] and chemiluminescent reactions.[2] They can decompose intramolecularly to stable singlet products by several processes such as ring closure, fragmentation, and disproportionation. Intersystem crossing (ISC) from the triplet to a singlet spin state may occur prior to (Scheme I) or concurrent with (Scheme II) chemical reaction of the triplet biradical. With the notable exception of the Closs and Doubleday[3] CIDNP study of Norrish type 1 acyl biradicals, very little is known about the mechanism of the crucial ISC step. It therefore seemed worthwhile to prepare various perinaphthalenediyls (1) and measure their absolute rate of ring closure. In this manner geometric variation in the biradicals might be minimized as substituent effects were examined. We herein report the results of such a study on the parent hydrocarbon biradical (**1a**) and its tetradeuterio derivative (**1b**).



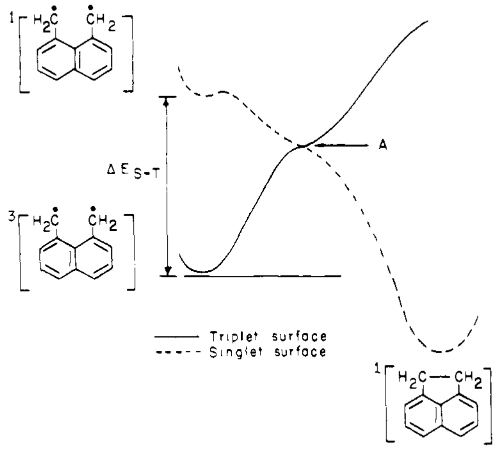
1

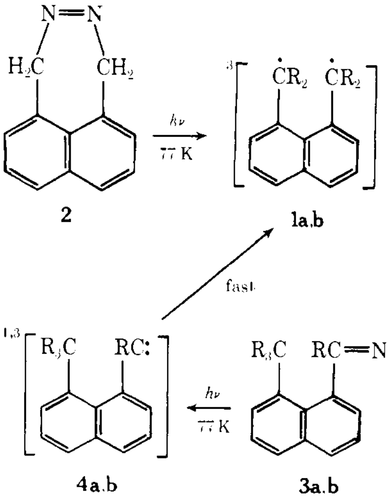
a, X = Y = CH_2; b, X = Y = CD_2

Scheme I



Scheme II





(a) R = H; (b) R = D

1,8-Naphthoquinodimethane was first observed by Pagni[4] by the photolysis of azo compound **2**. It can also be prepared by low-temperature photolysis of diazo compound **3** in 2-methyltetrahydrofuran (2MTHF) or hexafluorobenzene.[5] The hypothetical carbene intermediate **4a** was not observed, even at 4 K. As primary isotope effects may be exceptionally large at cryogenic temperatures, particularly if tunneling processes are involved, it was hoped that **4b** might be sufficiently long lived to afford ESR detection.[6] The synthesis of **3b** is shown in Scheme III (isotopic purity of the tosyl hydrazone, 75.6% d_4, 18.2% d_5, 3% d_6, and 4% d_7, as determined by mass spectroscopy). Photolysis of **3b** ($\lambda > 350$ nm) at 10 K produced a strong spectrum of the tetradeuterio biradical ($|D/hc| = 0.022$

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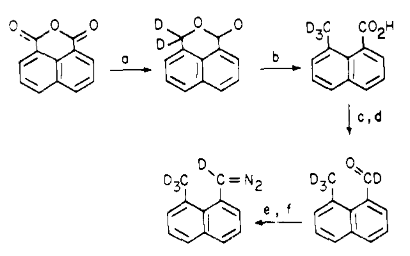
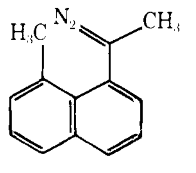
Scheme III^a

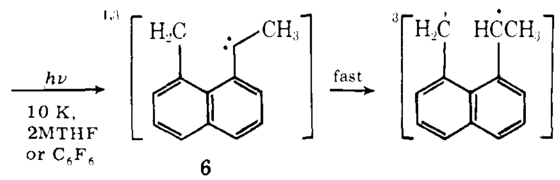


^{a}(a) LiAlD$_4$; (b) 10% NaOD, D$_2$O, D$_2$; (c) LiAlD$_4$; (d) MnO$_2$; (e) NH$_2$NH-SO$_2$-C$_7$H$_8$; (f) tetramethylguanidine.

± 0.001 cm^{-1}) ($|E/hc|$ = 0.0008 ± 0.0001 cm^{-1}), but again the carbene **4b** was not observed. Similarly, photolysis of **5** at 10 K gave rise to only a triplet biradical ESR spectrum.[7] In **6** 1,5-hydrogen migration was competitive with 1,2-carbon hydrogen insertion at low temperature.



5



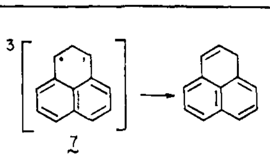
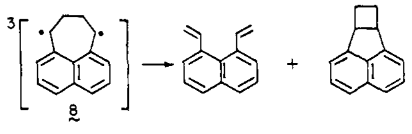
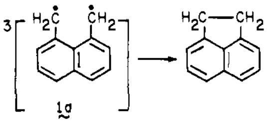
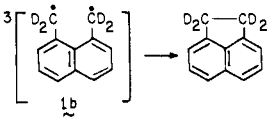
6

ESR kinetic techniques have been previously applied to other biradicals. Buchwalter and Closs studied the disappearance of 1,3-cyclopentadiyl[6] in this manner. Dowd and Chow have measured the Arrhenius parameters for the rate of ring closure of trimethylenemethane.[8] Muller et al. have also studied the reactions of biradical **7** by low-temperature ESR (see Table I). The lifetimes of **1a,b** in hexafluorobenzene were measured by the rate of disappearance of their respective ESR signals. Each rate constant was the average of at least four determinations and was first order for at least three half-lives.[9] The Arrhenius parameters for **1a** (see Table I) were determined over the temperature range 110-125 K (8 points). For **1b** the analysis was conducted between 118 and 134 K (7 points).

The data of Table I clearly indicates larger log A values for the reactions of **1a,b** than for those of **7** and **8**. However, the log A values do compare very favorably with those of Dowd and Chow[8] and Buchwalter and Closs.[6] The measurement of log A is relatively imprecise, particularly when determined over a small temperature interval. However, the differences in log A values observed between **1a,b**, **7** and **8** are far outside the experimental error. The data also indicates a larger energy of activation for reaction of **1a,b** than that for **7** and **8**. The difference in log A values between **1a,b** and **8** may arise from a medium effect (the decay of **8** was measured in fluid solution at elevated temperature). However, the decay kinetics of **7** were measured by low-temperature ESR. Therefore the difference in log A values of **1a,b** and **7** may not be due to environmental effects.

ISC may occur prior to[10] or concurrent with ring closure of the biradical. In the former case (Scheme I) the triplet biradical is upconverted into a low-lying excited singlet state of similar geometry. The singlet biradical then reacts to form a stable, singlet reaction product. Alternatively (Scheme II) ISC may occur concurrent with geometric distortion (rotation about the naphthalene-*exo*-methylene carbon-carbon bond).

Table I

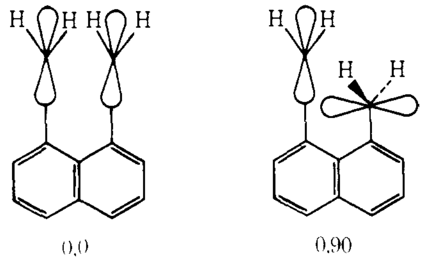
REACTION	log A sec^{-1}	ΔE_{act} ($\frac{kcal}{mole}$)	Ref
 **7**	4.5 ± 1	4.5 ± 0.6	a
 **8**	6.9 ± 0.3	4.5 ± 0.3	b
 **1a**	10.4 ± 0.5	6.4 ± 0.3	c
 **1b**	8.7 ± 0.7	6.0 ± 0.5	c

^{a} Reference 14. ^{b} Reference 15. ^{c} This work.

At point A, the singlet and triplet state surfaces become nearly degenerate. ISC from the triplet to the singlet surface can occur, followed by collapse to the singlet acenaphthene.

Pagni has shown that the singlet and triplet states of the ethano bridged biradical **8** are chemically distinct entities.[4] A dramatic change in product distribution obtained from **8** (1,8-divinylnaphthalene vs. 1,8-naphthocyclobutane) was observed upon variation of the reaction temperature. On the basis of these effects and other studies, Pagni and co-workers have concluded that the mechanism of Scheme I is operative in this system.

There is no corresponding chemical evidence in the parent system (**1a,b**) to indicate for, or against, the mechanism of Scheme I. The differences in log A values between **1a,b** and **8** may signal a change in mechanism. If one assumes the mechanism of Scheme II, the triplet-singlet surface crossing (point A) will be rate determining. The triplet-singlet surface crossing will also be rate determining in Scheme I, if ISC is much slower than subsequent reaction in the singlet manifold. Spin orbit coupling is known to facilitate ISC; however, not all geometric arrangements are equally effective. An orthogonal array of orbitals (0,90; 45,45, etc.) should be far more conducive to ISC than a parallel arrangement (0,0).[11] If ISC is rate determining for both **1a,b** and **8** (regardless of whether Scheme I or II is operative), the more orthogonal the biradical termini are at the respective surface crossing, the more efficient ISC will be and the larger the value of log A will be. This explains the larger log A value observed for the more flexible parent biradical **1a,b** than that observed for **8** which is constrained by an ethano linkage.[12] In fact, the parent biradical probably is already nonplanar in the triplet ground state, owing to steric interactions between the peri methylenes. Unfortunately, analyses of the ESR spectra of **1a,b** do not yield the degree of twisting.



0,0 0,90

Alternative interpretations of the log A data are possible.

One can account for the data by assuming that ISC is not rate determining for **1a,b**, but is rate determining for **8**:

$$^{3}[\mathbf{1a,b}] \xrightarrow{\text{fast}} {}^{1}[\mathbf{1a,b}] \xrightarrow{\text{slow}} \text{product}$$

$$^{3}[\mathbf{8}] \xrightarrow{\text{slow}} {}^{1}[\mathbf{8}] \xrightarrow{\text{fast}} \text{product}$$

This appears unlikely as no a priori reason for this change in mechanism is immediately apparent. Another interpretation of the data is that triplets **1a,b** cyclize to the excited triplet state of the acenaphthene.[13] This also appears unlikely as annealing a sample of **1a** in hexafluorobenzene from 77 K to room temperature, in a dark room, does not produce any visible emission.

Wirz has observed dramatic rate accelerations of the decay of **8** in the presence of heavy atoms.[15b] However, the effect of the matrix on the reactivity of **1a** is quite modest. At 110 K the rate constants of decay of **1a** in 2-methyltetrahydrofuran, hexafluorobenzene, and iodobenzene are 4.8 ± 0.3, 6.1 ± 0.3, and $7.1 \pm 0.3 \times 10^{-3}\ \text{s}^{-1}$, respectively. The lifetime of **1a** is not changed by the addition of styrene to 2MTHF. In biradical **8** the internal spin orbit coupling is efficient and ISC can be stimulated by an external heavy atom. When the internal spin orbit coupling is efficient, as in **1a**, the heavy-atom matrix provides little enhancement of ISC.

The relative lifetimes of **1a,b** at 118 K are $k_H/k_D = 6.7$. The isotope effect has its origin predominantly in the respective log A values. These results are reminiscent of isotope effects observed in photoexcited triplets, as perdeuteration substantially increases phosphorescent lifetimes (less efficient $T_1 \rightarrow S_0$ ISC).[16] Similar kinetic analyses of heteroatomic derivatives of **1a,b** are in progress.

Acknowledgment. The author thanks Professors J. Michl, R. Pagni, and J. Wirz for valuable discussions. Support of this work by the National Science Foundation (Grant No. CHE-7900896) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(7) $|D/\hbar c| = 0.023 \pm 0.002\ \text{cm}^{-21}$; $|E/\hbar c| = 0.001\ \text{cm}^{-1}$. **5** was characterized by oxidation of corresponding hydrazone with HgO. The hydrazone was characterized by its IR and mass spectra.

(8) Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6438–6440.

(9) Kinetic analysis of matrix reactions over several half-lives often correlates with $(\text{seconds})^{1/2}$ than seconds (see ref 6). The data of this work was simple first order for three half-lives. The quality of the data did not permit analysis of long reaction times.

(10) This is basically the mechanism proposed by Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317–5318.

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(12) The analysis presented herein does not require that the ISC of **1a** must occur from the idealized 0,90 or 45,45 geometry, or by a single or double rotation. The explanation requires only more rotation about the *exo*-methylene carbon–carbon bond in **1a,b** than for **7** or **8**.

(13) We thank Professor Jacob Wirz for bringing this interpretation to our attention.

(14) Muller, J. F., Muller, D., Dewey, H. and Michl, J., *J. Am. Chem. Soc.*, **1978**, *100*, 1629–1630.

(15) (a) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979** *101*, 2216–2218. (b) The lifetime of triplet **8** is reduced from 200 to 20 μs on changing the solvent to methylene bromide (see ref 15a).

(16) Hutchinson, C. A., Jr.; Magnum, B. W. *J. Chem. Phys.* **1961**, *34*, 908–922.

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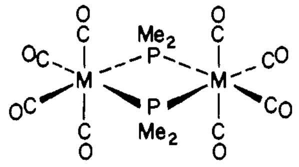
Why Some Binuclear Complexes Bridge, While Others, Even Though They Might Have a Quadruple Bond Available to Them, Do Not

Sir:

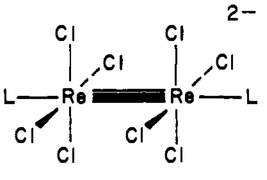
In 1978 Vahrenkamp reported a series of binuclear complexes $(CO)_4M(\mu\text{-}PMe_2)_2M(CO)_4$ (M = Mn, Cr, V) with edge-sharing bioctahedral structures, **1**.[1] A good structural case for an MM bond order of 0, 1, 2, respectively, was made. If the phosphido group is counted as PR_2^- one is led to oxidation state I for the metal, and the V complex is d^4–d^4.



1

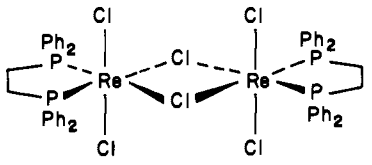
M	Mn	Cr	V
MM(Å)	3.76	2.90	2.73
MPM(°)	103.1	77.7	70.5

However, there are other d^4–d^4 dimers. These come from one of the most exciting chapters of modern inorganic chemistry, the work of Cotton and collaborators on metal quadruple bonding.[2] The classical example is $Re_2Cl_8^{2-}$; however, we know that two further weak axial ligands may add, giving a $Re_2Cl_8L_2^{2-}$ (**2**), which retains a short and strong bond.



2

Re–Re 2.22 Å



3

Re–Re 3.81 Å

The set of M_2L_{10} structures is not exhausted by these. There exist d^4–d^4 Re(III) dimers which have two bridging groups and *no* metal–metal bond. An example is the paramagnetic Walton complex **3**, $Re_2Cl_6(dppe)_2$,[3] whose Re–Re separation is nearly 1.6 Å longer than that in $Re_2Cl_8^{2-}$.

Thus there are three classes, at least, of d^4–d^4 M_2L_{10} complexes: (a) the Vahrenkamp compounds, bridged, diamagnetic, with medium-length MM bonds; (b) the Cotton structures, diamagnetic, short Re–Re distances, unbridged; (c) the Walton complexes, paramagnetic, long M–M distances, bridged. The basic structural question thrusts itself before our eyes. *What factor in the metal and ligand set makes a given M_2L_{10} d^4–d^4 complex assume one structure over another?* In particular, given the enticing prospect of a quadruple bond, why do the Vahrenkamp and Walton complexes not undo their bridging? Simply—*why do these complexes have the structures that they do?*

As part of a comprehensive study of M_2L_{10} dimers[4] we have

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