have constant intrinsic barriers.

In addition to these difficulties, there is at least a reasonable doubt that the conditions for the validity of eq 4 are met by electrophile–nucleophile combination reactions. If, as we believe probable,[2] extensive desolvation of reactants occurs before any appreciable bond formation, then there is no single extent of reaction variable and work terms[26] must be considered. There is a further indication of complications arising from different extents of reaction measured by resonance and polar effects[29] in some of these reactions. The additivity condition[30] is probably less troublesome.

It is clearly naive and speculative, at best, to attempt the application of eq 7 to reactions of the type of eq 8. Until some theory

of reasonable origin is developed that at least gives the coefficient of $\Delta G°$ in some rate–equilibrium relationship, attempts such as Albery's[13] to derive intrinsic properties from the measured rate and equilibrium constants by rearrangement of eq 7 are completely meaningless.

We suspect, on the basis of the approximately invariant orders of reactivities of nucleophiles and electrophiles seen in a number of studies of the combination reactions,[2,3] that some intrinsic contributions to the reaction barriers exist. We also believe, as stated in the introduction, that the free energies of activation contain some contributions from the same factors that influence the free energies of reaction. At present, however, we have no way of separating these contributions.

Acknowledgment. This work was supported by Grant GM-12832 from the National Institutes of Health, U.S. Public Health Service. We are grateful to Prof. J. P. Guthrie for criticisms of early drafts of this paper, which have forced us to clarify our arguments.

(29) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288. Young, P. R.; McMahon, P. E. *Ibid.* **1979**, *101*, 4678.

(30) Such additivity, at least at the transition states, is clearly implied by the N_+ relationship (ref 2). There can be no doubt that additivity applies to the reactants, where E and N are independent entities.

Effects of Through-Bond and Through-Space Interactions on Singlet–Triplet Energy Gaps in Localized Biradicals

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Abstract: Singlet–triplet energy gaps in localized 1,3 biradicals have been investigated by using ab initio electronic structure theory. Analysis of both the molecular orbital and generalized valence bond wave functions allows one to follow the complex interplay between through-bond and through-space interactions. When the two effects are of similar magnitude, a triplet ground state is possible. However, when one significantly dominates the other, a singlet ground state is expected. Extension of the analysis to other systems and the implications of the results for experimental studies of localized biradicals are discussed.

Biradicals have long been postulated as intermediates in a variety of thermal and photochemical reactions.[1] More recently, direct observations of such species has become possible, and ESR studies of several highly delocalized biradicals have been reported over the last 15 years.[2] In 1975, Closs[3] photolyzed azoalkane 2 at 5.5 K and observed the ESR spectrum of the triplet state of
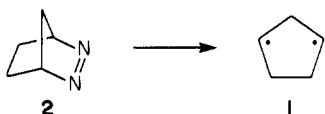
1,3-cyclopentanediyl (**1**). This landmark result promised to remove simple *localized*[4] biradicals from the realm of "permissible

intermediate" and "theoretical model" to that of thermodynamically and kinetically characterized reactive intermediate. However, extension of the Closs experiment to other fundamental localized biradical systems has thus far not been possible. This failure is certainly not for want of effort,[3,5,6] and it suggests that insights into the factors that make the observation of **1** successful would be useful.[7]

Several lines of experimental evidence[3] and theoretical calculation[8] indicate that **1** has a triplet ground state. It seems certain that this is a major factor that facilitates its direct observation by ESR. Direct observation of the singlet state of a localized biradical has not yet been accomplished, and in most cases the lifetimes of such species must be quite short. If a biradical has a triplet ground state, however, the spin forbiddenness of the normal unimolecular decomposition pathways (e.g., ring closure) can increase the biradical lifetime. If the singlet–triplet energy gap is substantial, an additional enthalpic barrier to the T → S conversion may also be operative. It is quite possible that a triplet ground state is a necessary criterion for ESR observation of certain types of nonconjugated biradicals. In the general case, however, one would not expect a triplet ground state for a localized biradical. Hund's rule does not apply to structures such as **1**, since the atomic orbitals containing the unpaired electrons are not orthogonal.[9]

(1) (a) Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, pp 311–390. (b) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981. (c) Wagner, P. J. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press, New York, 1980; Vol. III, pp 381–444. (d) Borden, W. T., Ed. "Diradicals"; Wiley-Interscience: New York, 1982.

(2) (a) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587–2589. (b) Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *Ibid.* **1967**, *89*, 3376–3377. (c) Arnold, D. R.; Evnin, A. B.; Kasai, P. H. *Ibid.* **1969**, *91*, 784–785. (d) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *Ibid.* **1971**, *93*, 1544–1546. (e) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503–504. (f) Pagni, R. M.; Watson, C. R., Jr.; Boor, J. E.; Dodd, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 4064–4066.

(3) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688–4694.

(4) The term "localized" is used here in a classical sense, implying that the radical centers are not part of a conventional π system. Of course, a major point of this work is that the radical centers do delocalize via the CH_2 groups.

(5) Goldberg, A. H.; Dougherty, D. A., unpublished results.

(6) Closs, G. L., personal communication.

(7) Of course, one must have a suitable photochemicl precursor, and it is quite possible that in some cases the photochemistry of the biradical precursor undermines the experiment (see below).

(8) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1979**, *101*, 2245–2246.

Also, a weakly interacting pair of radicals does not generally exhibit a triplet ground state, as evidenced by the fact that S_0 always remains below T_1 in the homolytic dissociation of H_2.[10]

The present work was therefore undertaken to determine why **1** has a triplet ground state. While the ESR experiment on **1** provided the major impetus for this work, localized triplet biradicals have more recently been observed directly by using laser flash photolysis techniques[11] and indirectly by CIDNP.[12] Clearly, knowledge of the factors that determine ground-state spin multiplicity would be quite useful in designing and interpreting such experiments. This is especially so since singlet–triplet energy gaps greatly influence intersystem crossing rates and thus significantly affect the lifetime and chemistry of biradicals and excited states in general.[13]

Our calculations reveal that the through-space interaction between the radical orbitals in **1** is surprisingly large, but it is almost exactly counteracted by an equally large through-bond effect. Under such circumstances a triplet ground state can develop. In addition to quantifying the interactions in **1** and related molecules, we have analyzed the generalized valence bond (GVB) wave functions[14] for such structures. The GVB approach provides a simple, alternative model for the interplay between through-bond and through-space interactions, and we have used it as a basis for the extension of our results for **1** to other systems.

Computational Methods

All calculations were performed by using a valence double-ζ basis set. For carbon, Dunning's contraction[15] (3s,2p) of Huzinaga's (9s,5p) basis set[16] was adopted, while for hydrogen a comparable (4s/2s) contraction was utilized,[15] with each Gaussian exponent scaled by a factor of 1.44.

Wave functions for triplet biradicals were obtained by using restricted Hartree–Fock (RHF) theory. However, an MCSCF procedure,[17] in which both the orbitals and their mixing coefficients were simultaneously optimized, was employed to yield a two-configuration wave function for each singlet. This level of theory has been shown to weight ionic and covalent terms properly[18] and has been successfully employed in several recent studies of localized biradicals.[8,19] At this level, the triplet state of **1** lies 0.9 kcal/mol below the singlet.[8]

Our confidence in the reliability of this level of theory is further enhanced by the fact that more extensive CI calculations on **1** lead to only minor changes in the singlet–triplet gap. For example, we have found that allowing all single and double excitations from the five π orbitals (obtained separately for each state, as described

above) into the π virtual space increases the singlet–triplet gap to 1.15 kcal/mol.[20]

It should be emphasized from the start that quantitative prediction of singlet–triplet gaps is not the goal of the present work. We are principally interested in trends in the data and the underlying factors responsible for them. Even if the calculations are only semiquantitatively accurate, we believe they should be adequate for this purpose.

Results and Discussion

Before presenting our results, we shall briefly review the molecular orbital (MO) analysis of simple biradicals such as **1**.[18] Such structures are homosymmetric biradicals in that the two p orbitals that contain the odd electrons are interconvertible by a symmetry operation of the molecule. Through-space overlap of these orbitals leads to two formally nonbonding MO's (NBMO): one symmetric with respect to a mirror plane and slightly bonding (S), the other antisymmetric and slightly antibonding (A). Energetically, S lies below A.

As first noted by Hoffmann,[21] the intervening methylene group (C2) in **1** provides a pair of orbitals—one bonding (π_{CH_2}), one antibonding ($\pi^*_{CH_2}$)—that can interact with the biradical orbitals. The A molecular orbital is prevented by symmetry from mixing with either of these orbitals, but the S molecular orbital can mix with both. Interactions with the π_{CH_2} orbital increase the energy of the biradical S orbital, while interactions with the $\pi^*_{CH_2}$ orbital decrease the energy. Generally, the former effect dominates, either because of a smaller energy gap between the orbitals or because of better overlap.[22] Since through-space effects place the S MO below the A MO, through-bond interactions can substantially diminish the S–A energy gap. However, if the through-bond interactions are much greater than the through-space effect, the magnitude of the S–A gap can actually increase, albeit with A below S.

The two MO's described above can be used to construct wave functions for the triplet and singlet states. In the high-spin species, the two electrons must occupy different orbitals, resulting in a simple, single-determinant wave function (eq 1). Only for such

$$^3\psi_{RHF} = (2)^{-1/2}(\phi_S\phi_A - \phi_A\phi_S)(\alpha\alpha) \qquad (1)$$

a wave function does the term "orbital energy" have its usual meaning, and subsequent discussions of S–A energy gaps will always refer to triplet wave functions. For the singlet state three configurations are possible: $\phi_S\phi_S$, $\phi_S\phi_A$, and $\phi_A\phi_A$. One of these ($\phi_S\phi_A$) is forbidden by symmetry from mixing with the other two, and the lowest singlet is best described by the two-configuration MCSCF wave function (eq 2).[18] The orbitals for this state must

$$^1\psi_{MCSCF} = (C_1^2 + C_2^2)^{-1/2}(C_1\phi_S\phi_S - C_2\phi_A\phi_A)(\alpha\beta - \beta\alpha)$$
$$C_1, C_2 > 0$$
$$(2)$$

be optimized separately. Thus, in eq 2, ϕ_S and ϕ_A are the "natural orbitals", and their form very closely parallels that of the triplet MO's. The weighting of the configurations in this CI wave function is determined, for the most part, by the orbital energies. The configurations involving double occupation of the lower energy orbital will generally have the larger CI coefficient, and the two configurations will have equal coefficients if the orbitals are degenerate.

The value of the singlet–triplet gap (ΔE_{S-T}) depends upon two factors: (1) the energy difference between the S and A orbitals, with a large gap favoring the singlet, and (2) the exchange re-

(9) Hund, F. *Z. Phys.* **1925**, *33*, 345–371. A new interpretation of Hund's rule, in terms of anisotropic screening effects, has recently been offered: Shim, I.; Dahl, J. P. *Theor. Chim. Acta* **1978**, *48*, 165–174.

(10) S_0 remains below T_1 at all distances, even in much more sophisticated calculations: Kolos, W.; Wolniewicz, L. *Chem. Phys. Lett.* **1974**, *24*, 457–460. Alexander, M. H.; Salem, L. *J. Chem. Phys.* **1967**, *46*, 430–439.

(11) (a) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431–434. (b) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828–832. (c) Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1977**, *81*, 2126–2131.

(12) (a) Doubleday, C., Jr. *Chem. Phys. Lett.* **1979**, *64*, 67–70. (b) Doubleday, C., Jr. *Ibid.* **1981**, *77*, 131–134. (c) Doubleday, C., Jr. *Ibid.* **1981**, *79*, 375–380.

(13) Small singlet–triplet gaps generally lead to rapid intersystem crossing rates due to favorable Franck–Condon factors. See, for example: Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(14) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368–376 and references cited therein.

(15) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823–2833.

(16) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293–1302.

(17) All Hartree–Fock and two-configuration SCF (i.e., GVB (1)) calculations were performed by using the MQM:GVB2P5 program: Bair, R. A.; Goddard, W. A., III, unpublished work. Bair, R. A. Ph.D. Thesis, California Institute of Technology, 1982. Bobrowicz, F. W.; Goddard, W. A., III. In "Methods of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; pp 77–127.

(18) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.

(19) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 5409–5410.

(20) The CI calculations was carried out by using the MQM:CI2P5 program: Bobrowicz, F. W.; Goodgame, M. M.; Bair, R. A.; Walch, S. P.; Goddard, W. A., III, unpublished work. Bobrowicz, F. W., Ph.D. Thesis, California Institute of Technology, 1974.

(21) (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (b) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

(22) Overlap appears to be the factor most responsible for favoring interactions with the π_{CH_2} orbital: Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976**, *98*, 4392–4393.
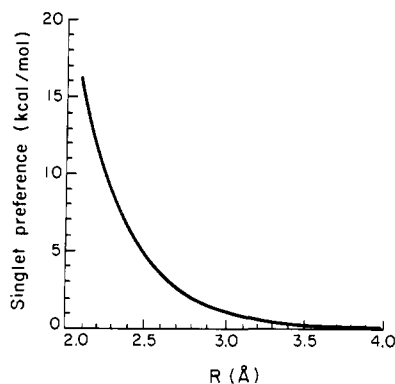
Figure 1. Singlet–triplet energy gap as a function of internuclear separation R for two weakly interacting methyl radicals (3).

pulsion energy, which favors the triplet. The orbital energy gap will be large whenever either the through-space or the through-bond interaction dominates the other. In such cases a singlet ground state is expected. However, when the two effects are of comparable magnitude, a small S–A gap results. In this case it is difficult to predict the ground-state multiplicity, but a triplet ground state is at least feasible.[18]

Through-Space Interactions. We have modeled the through-space interactions[21] in localized biradicals such as 1 by considering two adjacent methyl radicals interacting in a π fashion (3, D_{2h} symmetry).[23] The results are shown in Figure 1. At all sepa-

3
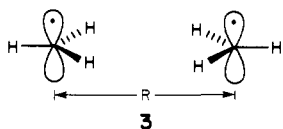
rations R, the radical pairs assume a singlet ground state. Evidently, the S–A gap dominates over the exchange repulsion even when R is large—just as in the case of H_2. What could be considered surprising about Figure 1 is the magnitude of the singlet preference. At a distance of 2.37 Å, corresponding to the separation in 1,[8] singlet coupling is favored by a full 7.2 kcal/mol.

A useful, alternative analysis of such interactions is provided by GVB theory, in which the radical electrons are confined to different orbitals that are optimized self-consistently.[14] The resulting GVB orbitals tend to localize on separate centers so that electron repulsions can be minimized. At the same time, these "left" and "right" orbitals (ϕ_l and ϕ_r) also build in some density at the opposite centers. In this way, each one can reduce its kinetic energy without significantly affecting nuclear–electron attractions. A typical GVB pair is shown in Figure 2.

Singlet and triplet pairing of the GVB orbitals lead to wave functions 3 and 4, respectively. It can easily be shown that the

$$^1\psi_{GVB} = (2 + 2\,S_{lr}^2)^{-1/2}(\phi_l\phi_r + \phi_r\phi_l)(\alpha\beta - \beta\alpha) \qquad (3)$$

$$^3\psi_{GVB} = (2 - 2\,S_{lr}^2)^{-1/2}(\phi_l\phi_r - \phi_r\phi_l)(\alpha\alpha) \qquad (4)$$

singlet GVB wave function is equivalent to the MCSCF wave function (eq 2), where the GVB orbitals are related to the natural orbitals by eq 5. The GVB-pair overlap (S_{lr}) is given by eq 6.

$$\phi_l = (C_1^{1/2}\phi_S + C_2^{1/2}\phi_A)/(C_1 + C_2)^{1/2}$$
$$\phi_r = (C_1^{1/2}\phi_S - C_2^{1/2}\phi_A)/(C_1 + C_2)^{1/2} \qquad (5)$$

$$S_{lr} = \frac{C_1 - C_2}{C_1 + C_2} \qquad (6)$$

The GVB orbitals are separately optimized for the triplet, and $^3\psi_{GVB}$ and $^3\psi_{RHF}$ can also be related by eq 5, with both C_1 and

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(23) The C–H bond lengths in the two methyl radicals were chosen to be 1.09 Å.
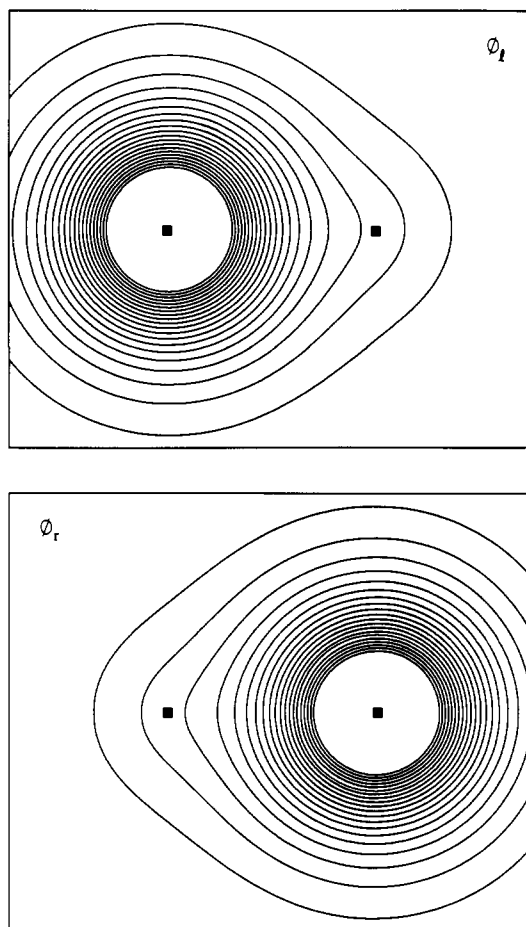
Figure 2. GVB orbitals for two methyl radicals (3) at a distance of 2.37 Å. Contours indicate amplitudes of the orbitals 0.89 Å above the atomic plane. The increment between contours is 0.005 au. Amplitudes above 0.1 au have been omitted.

C_2 (which no longer represent CI coefficients) equal to 0.5. Notice that in this case, the overlap between the orbitals (S_{lr}) is zero (eq 6).

While eq 4 is the true high-spin GVB wave function, the triplet may be more conveniently approximated in the present systems by replacing the triplet-optimized ϕ_l and ϕ_r by the corresponding *singlet* GVB orbitals. This simplification allows each state to be described by a single-configuration wave function involving the same set of orbitals, and this constitutes a major advantage of the GVB analysis of such wave functions. It also leads to a simple expression for ΔE_{S-T} (eq 7),[24] where h, J, and K are, respectively,

$$\Delta E_{S-T} = E^1_{GVB} - E^3_{GVB} =$$
$$(4S_{lr}h_{lr} - 2S_{lr}^2h - 2S_{lr}^2h_{rr} - 2S_{lr}^2J_{lr} + 2K_{lr})/(1 - S_{lr}^4) \qquad (7)$$

the one-electron, Coulomb, and exchange integrals over the GVB orbitals. The first four terms in the numerator of eq 7 all depend explicitly on S_{lr}. Taken together, these terms are negative, so that increasing the overlap of the GVB pair favors the singlet. The fifth term, $2K_{lr}$, is always positive and thus favors the triplet. This result is in agreement with one's usual chemical intuition: a large overlap between the left and right orbitals indicates a bonding interaction and a strong preference for singlet spin multiplicity.

For the interaction in 3, the GVB orbital overlap is quite large

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(24) This is actually the value for the "triplet excitation energy". The true value of ΔE_{S-T} is obtained when the orbitals for each state (including the core orbitals) are optimized separately. In the present systems, however, eq 7 very closely approximates ΔE_{S-T}.

Figure 3. Singlet–triplet energy gap as a function of central angle θ in (0,0)-trimethylene (**4**). Positive values indicate a singlet ground state.

at short distances and a singlet ground state results. Increasing R decreases both S_{lr} and K_{lr}. Apparently, S_{lr} predominates at long distances just as it does at short distances, and the radical pair always remains a singlet. Thus, the MO and GVB analyses of through-space effects are quite similar.
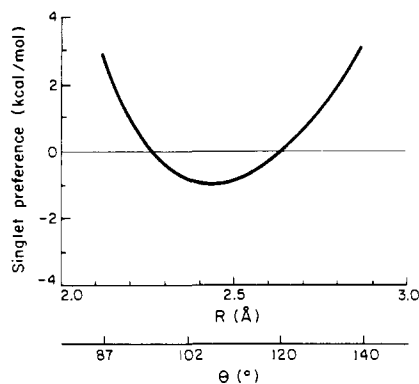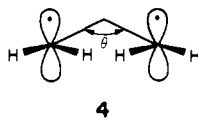
Through-Bond Interactions in (0,0)-Trimethylene (4). In order to model the interplay between through-space and through-bond effects, we have studied (0,0)-trimethylene (**4**) as a function of

4

the C–C–C valence angle θ. This species has been extensively studied theoretically,[21,25] although the singlet–triplet energy gap (ΔE_{S-T}) has not been a major emphasis of these investigations. As will be shown below, **4** serves as an excellent model for **1**.

Figure 3 demonstrates that ΔE_{S-T} in **4** is strongly dependent on θ. The singlet is preferred at very large and very small values of θ, while intermediate values lead to a triplet ground state.

Table I lists S–A orbital energy gaps for **3** and **4** as a function of R. The difference between these values is a reasonable estimate of the effect of through-bond coupling on the S–A gap. Clearly the dominant factor responsible for the variation in the S–A gap in **4** is the through-space overlap. To a first approximation, the through-bond effect is constant at 0.06 hartree, and the S–A gap in **4** can be obtained by simply destabilizing the S orbital in **3** by this amount. Closer inspection reveals that the through-bond effect actually increases monotonically with increasing θ. This is most likely a consequence of the fact that the coupling orbital at C2 is distorted toward the hydrogens, and thus overlap with the radical orbitals is greater at larger values of θ.

The region in which **4** has a triplet ground state corresponds to the region of a small S–A gap. However, just a small S–A gap is not enough to produce a triplet ground state (Figure 1). Clearly, exchange repulsions must be substantial in such structures. This conclusion can be rationalized by extending Borden and Davidson's elegant treatment of singlet–triplet energy gaps in highly delocalized biradicals containing degenerate NBMO's.[26] For the through-space interaction in localized biradicals, one can take appropriate linear combinations of the S and A orbitals and convert the NBMO's into two isolated p orbitals. Thus, exchange repulsions in the singlet are small, and a singlet ground state is feasible. However, when the NBMO's of **4** are similarly treated, the through-bond coupling unit must always be present in each linear combination. As a result, exchange repulsions remain substantial in the singlet. In the structures studied by Borden and Davidson, such an effect necessarily induces a triplet ground

Table I. S-A Gaps and GVB Overlaps for 3 and 4

		S-A Gap (hartree)			S_{ir}		
R, Å	θ,[a] deg	3[b]	4[b]	difference[c]	3	4	difference[c]
2.12	87	0.085	0.031	0.054	0.299	0.160	0.139
2.25	95	0.069	0.011	0.058	0.240	0.086	0.154
2.37	102	0.057	−0.003	0.060	0.206	0.032	0.174
2.50	110	0.047	−0.016	0.063	0.164	−0.019	0.183
2.64	120	0.037	−0.030	0.067	0.132	−0.068	0.200
2.87	140	0.025	−0.051	0.076	0.092	−0.141	0.233

[a] Value of θ in **4** that leads to the value of R shown. [b] A positive value indicates S below A. [c] Value for **3** minus the value for **4**.

state.[26] In **4**, however, the NBMO's are not forced to be degenerate. Only when the through-bond and through-space effects nearly balance one another and the NBMO's are nearly degenerate does a triplet ground state result.

It seems likely that the more effective the through-bond coupling unit, the greater the exchange repulsions between NBMO's and the greater the potential for a triplet ground state. In this light, D_{3h} trimethylenemethane (**5**) can be viewed as a (0,0)-trimethylene

5
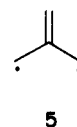
with an especially effective through-bond coupling unit. Since the NBMO's of **5** are degenerate and "through-bond interactions" are quite large, a substantial energetic preference for the triplet ground state results.[26,27]

In GVB terms, when a through-bond coupling unit is introduced into a system, both ϕ_l and ϕ_r must become orthogonal to it.[14] As first pointed out by Goddard,[14] this is accomplished by incorporating the coupling unit *out of phase*, thus introducing a nodal surface into the GVB orbitals (Figure 4). The sign at the "far" center in each orbital is then determined by a competition between through-space interactions, which favor having the two ends in phase, and the need to minimize one-electron energies. The latter effect favors having the "far" lobe in each orbital in phase with the through-bond coupling unit (i.e., out of phase with the main lobe).

When θ is small, through-space overlap in **4** is large and the first effect dominates (Figure 4a). However, when θ is large, the second effect is more important, and the radical centers are out of phase in each GVB orbital (Figure 4c). Thus, the position of the nodal surface changes in response to the variation in θ. At intermediate values, the node passes almost directly through the far center (Figure 4b).

The way in which the GVB orbitals change with geometry has important implications on the extent to which they overlap with each other (Table I). If, by convention, the orbitals at C1 in ϕ_l (C1(l)) and C3 in ϕ_r (C3(r)) are assigned to be in phase (Figure 4), the contribution to the overlap of the GVB pair (S_{lr}) from the region of the through-bond coupling unit must be positive. The more important overlap, however, occurs where the AO coefficients are largest, and this is at the radical centers.[28] For small θ, C1(l) and C3(l) are in phase, and thus C1(l) and C1(r) must also be in phase. Therefore, the GVB-pair overlap at the radical centers reinforces the positive overlap at the through-bond coupling unit. As the central angle is opened (Figure 4b), C1(l) and C3(l) become out of phase with respect to one another, and thus so do C1(l) and C1(r). The GVB-pair overlap at the radical centers becomes negative, and this counterbalances the positive overlap at the

(25) (a) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 638–640. (b) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *Ibid.* **1972**, *94*, 279–282.

(26) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594.

(27) This result is borne out by experiment[2a] and quantitative theoretical calculations: Yarkony, D. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1974**, *96*, 3754–3758. Davis, J. H.; Goddard, W. A., III *Ibid.* **1977**, *99*, 4242–4247.

(28) There is ample precedent for the end overlaps being most important: Hay, P. J., Ph.D. Thesis, California Institute of Technology, 1972; pp 68–71.
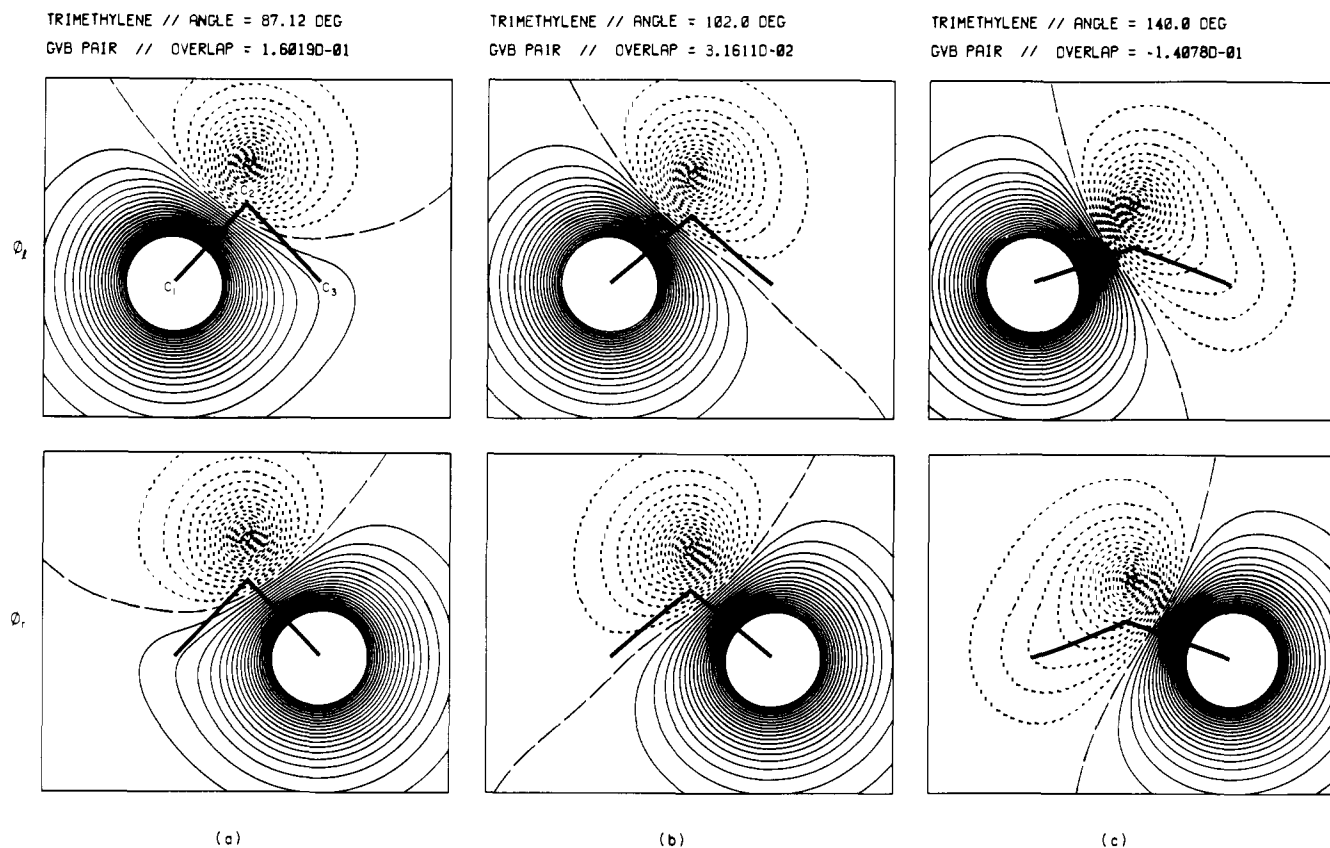
TRIMETHYLENE // ANGLE = 87.12 DEG
GVB PAIR // OVERLAP = 1.60190-01

TRIMETHYLENE // ANGLE = 102.0 DEG
GVB PAIR // OVERLAP = 3.16110-02

TRIMETHYLENE // ANGLE = 140.0 DEG
GVB PAIR // OVERLAP = -1.40780-01

(a)   (b)   (c)

Figure 4. GVB orbitals for three geometries of (0,0)-trimethylene (**4**) plotted as in Figure 2. Long dashes indicate nodes while solid lines and short dashes indicate positive and negative amplitudes, respectively.

through-bond coupling unit. The overall magnitude of S_{lr} is thus diminished and eventually S_{lr} goes to zero. Upon further expansion of θ, the negative overlap at the radical centers overwhelms the positive overlap at C2, leading to a large, negative S_{lr} (Figure 4c). The sign of the overlap, of course, has no true physical meaning. Thus, one is left with the counterintuitive result that increasing the distance between the radical centers can actually increase the GVB-pair overlap.

The quantitative trend in S_{lr} with varying θ is shown in Table I. At all values of θ, S_{lr} in **4** is much less than in **3**, as a result of through-bond coupling. As in our earlier analysis of the S–A MO energy gap, the difference in S_{lr} between **3** and **4** can be taken as a measure of the effectiveness of through-bond coupling. The data indicate that through-bond coupling is more effective at larger values of θ, again suggesting an enhanced overlap with C2 at large values of θ.

Given the above analysis, it is now possible to consider the state splitting in trimethylene. Whenever the GVB overlap is large (greater than approximately 0.1), the singlet state should be lower in energy. This is precisely the case for $\theta = 87°$ or 140° (Figure 3). At intermediate angles, S_{lr} approaches and ultimately reaches zero. However, K_{lr} does not go to zero like it did in the through-space model system (**3**). This is because, when S_{lr} is diminished by special nodal properties of the GVB orbitals (as it is with through-bond coupling), the $1/r$ term in K_{lr} necessarily leads to a finite positive value for the integral.[29] A triplet ground state thus results.

The similarity of the roles of S_{lr} in GVB theory and the S–A gap in MO theory is apparent. If either is diminished in absolute value by simply separating the radical centers, exchange repulsions are similarly diminished and a singlet ground state results. However, if special characteristics of the wave function cause S_{lr} or the S–A gap to fortuitously go to zero, the exchange repulsions can still be significant and a triplet ground state may result. The reason for this parallel behavior is made clear with reference to eq 6. S_{lr} will be large whenever $|C_1 - C_2|$ is large, and, as discussed above, $|C_1 - C_2|$ will be large whenever the S–A gap is large. Note

that just as Hund's rule for atoms predicts that whenever two electrons occupy two orthogonal orbitals on the same atomic center, the high-spin state is preferred, so the GVB analysis of molecules predicts that whenever the GVB-pair orbitals occupy the same region of space and are orthogonal, or nearly so ($S_{lr} \approx 0$), the high-spin state is preferred.

Trimethylene Derivatives. The discussion of **4** can easily be adapted to other 1,3-biradical systems. Several studies[19,30] have shown that ethano bridges are poor through-bond couplers. One would therefore expect that Closs' biradical (**1**) would resemble **4**, with the appropriate value of θ (102°).[8] Indeed, we find that the state splittings in **1** and **4** ($\theta = 102°$) are 0.85 and 0.88 kcal/mol, at the current level of theory. Our original question concerning the reason for the triplet ground state in **1** is therefore answered.

In an attempt to observe the closely related structure 1,3-cyclobutanediyl (**6**), we have recently photolyzed azoalkane **7**[31] at 8 °K in a variety of matrices. However, we have been unable

7   **6**
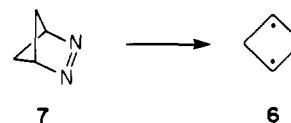
(29) As shown below, the exchange integral K_{lr} depends explicitly on the overlap *function f*, as opposed to the overlap *integral* S_{lr}, which is the integral of *f* over all space. At intermediate geometries of (0,0)-trimethylene, even

$$K_{lr} = \int \int \phi_l(1)\phi_r(1)(1/r_{12})\phi_l(2)\phi_r(2) \; d\tau_1 d\tau_2 =$$

$$\int \int f(1)(1/r_{12})f(2) \; d\tau_1 d\tau_2$$

though S_{lr} approaches zero, *f* does not. The integrand of K_{lr} is positive whenever $f(1)$ and $f(2)$ have the same sign and negative when they are oppositely signed. Most importantly, the integrand is, in general, positive when the $1/r$ term is greatest—namely when the two electrons are in the same region of space. Because of this fact, K_{lr} will be positive even when S_{lr} is zero.
(30) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878–2880.
(31) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092–4093.

Through-Bond and Through-Space Interactions

J. Am. Chem. Soc., Vol. 105, No. 2, 1983 289

to observe any ESR signal corresponding to **6**. Our calculations offer some insight into the reason for this failure. A reasonable geometry for **6**[32] gives a C1···C3 distance of 2.12 Å. From Figure 1, one can see that through-space effects at this distance lead to a singlet ground state, with the triplet a full 15.4 kcal/mol higher. Thus a fairly strong π bond would exist in **6** if just through-space effects were operative. Through-bond coupling would be expected to oppose this π bond. Figure 3 shows that at the geometry corresponding to **6**, (0,0)-trimethylene is also a singlet, but through-bond coupling has reduced the gap to 2.9 kcal/mol. Calculations on **6** itself reveal that the second methylene bridge further cancels the through-space effect, and the triplet becomes the ground state by 1.7 kcal/mol ($S_{lr} = 0.004$). Thus, our failure to observe **6** is not due to a singlet ground state but more likely reflects the triplet photochemistry of **7**.[33] It would be interesting to devise alternative precursors to **6**, and to design structures analogous to **6** but with very weak through-bond coupling units, to test for the existence of the π bond.

It is interesting in the present context to examine the inorganic biradical ozone (**8**), which is isoelectronic with **4**. For a given
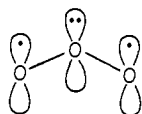
8

separation, oxygen p orbitals overlap less effectively than carbon orbitals, since they are more tightly held to the nucleus. Still, oxygen-centered radical pairs analogous to **3** exhibit singlet ground states.[34] Introduction of the central atom in **8** forces the two radical orbitals to become orthogonal to the central lone pair, which serves as a highly effective through-bond coupling unit.[14] The result, as in the case of **4**, is a more negative value of S_{lr}. Since the system starts with only a very small overlap and the through-bond coupling is quite effective, the final absolute value of S_{lr} is large. Ozone thus has a strong preference for singlet spin multiplicity.[14,35]

Other Systems. The approach described above for 1,3 biradicals can also be used to analyze other biradical systems. To illustrate this point, we shall consider the case of *trans*-(90,90)-tetra-methylene (**9**).[19,36] It should be clear that similar reasoning can be applied to other systems.
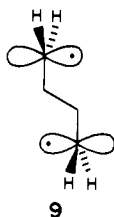
9

Each GVB orbital arising from two methyl radicals interacting in the tetramethylene geometry[19,36] is essentially an atomic p orbital localized at one of the radical centers.[37] The overlap of the two GVB orbitals is quite small ($S_{lr} = 0.003$). However, this result is due not only to the substantial distance between the centers but also to the nodal properties of the orbitals. In fact, increasing

(32) The geometry of the carbon framework was assumed to be identical with that in 1,3-dimethylenecyclobutane: Hemmersbach, P.; Klessinger, M.; Bruckmann, P. *J. Am. Chem. Soc.* **1978**, *100*, 6344–6347.

(33) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333–2334.

(34) The oxygen-centered radicals chosen for study were hydroxyl radicals. The calculations were performed with a double-ζ basis set.[15,16]

(35) Closing down the central angle in ozone should make the triplet lower in energy than the singlet. However, another higher lying state becomes the ground state as this distortion is made: Hay, P. J.; Dunning, T. H., Jr.; Goddard, W. A., III *J. Chem. Phys.* **1975**, *62*, 3912–3914.

(36) Segal, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 7892–7898.

(37) There is a small amount of residual through-bond coupling through the C–H bonds, but this effect is negligible.

TETRAMETHYLENE

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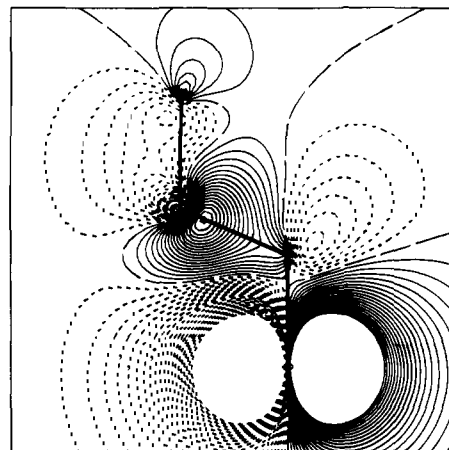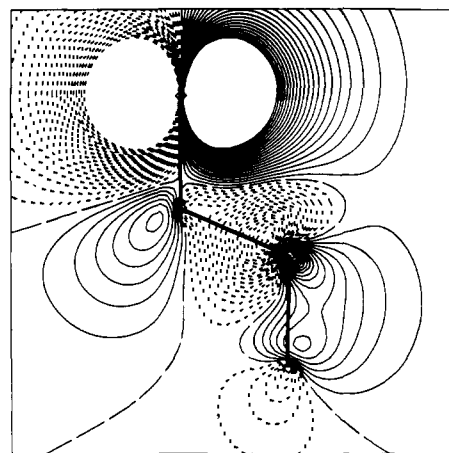
Figure 5. GVB orbitals for *trans*-(90,90)-tetramethylene (**9**). Contours are in the plane of the carbon atoms, with plotting conventions as in Figures 2 and 4.

the radical separation by moving one p orbital along its axis yields an overlap that is *larger* in magnitude. The reason for this apparent paradox can be seen in structures **10–12**. In **10**, two p
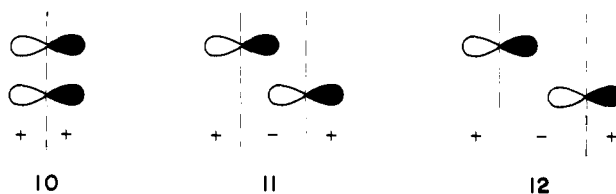
orbitals are aligned in an appropriate arrangement for a π interaction. The nodes of the orbitals coincide, and the overlap is positive throughout all regions of space. As one of the p orbitals is moved along its axis (**11–12**) a region of negative overlap is introduced between the two nodes. In **12**, this negative overlap is greater than the positive overlap, indicating that the interaction is predominately σ in nature. Our calculations reveal that the through-space interactions in **9** correspond to structure **11**, which is in the transition region between σ and π interactions. The very small through-space overlap thus results in part from a cancellation of overlaps. Since the nodal properties of the orbitals contribute significantly to their low overlap, one might expect that the exchange repulsions should predominate over S_{lr}, just as they did for the nearly orthogonal GVB orbitals of trimethylene with $\theta = 102°$. The radical pair would then exhibit a triplet ground state. Calculations reveal that this is, in fact, the case, but ΔE_{S-T} is very small (0.07 kcal/mol) because the large separation of the radical centers forces K_{lr} to be small. Of course, this level of theory is

not reliable for such small energy differences, but the results do illustrate an alternative mode by which triplet ground states can, in principle, be obtained.

Introduction of the C2–C3 bond as a through-bond coupling unit in **9** once again causes each GVB orbital to incorporate that element in an antibonding way (Figure 5). This induces a small contribution from the far centers, which are included in such a way as to minimize one-electron energies. Since there is no significant through-space overlap, the net result can only be an increase in $|S_{lr}|$. It is worth noting that the sign of the overlap between the orbitals, as drawn in Figure 5, is positive, even though the overlap at the C2–C3 bond is negative. Evidently, the most important overlap occurs at the "ends" of the biradical, just as in the case of trimethylene (**4**). Because of the enhanced overlap from through-bond coupling in **9**, the system prefers the singlet state by 0.53 kcal/mol at the present level of theory. A recent study at the same level of theory but with an STO-3G basis set found that **9** has the largest singlet–triplet energy gap of any of the idealized forms of *trans*-tetramethylene.[19] The (0,90) form, in which the two p orbitals are orthogonal, has a very small preference for the triplet state, for reasons analogous to Hund's rule.[19] The (0,0) form, on the other hand, shows a very small preference for the singlet[19] because the ethano bridge is a very weak through-bond coupler.

Conclusion

It is now clear which factors are necessary for a simple biradical to have a triplet ground state. From eq 7, the most general requirement is that $|S_{lr}|$ must be significantly smaller than K_{lr}. This can only be accomplished when S_{lr} is diminished by a cancellation of positive and negative regions of overlap,[29] rather than by a general reduction in overlap throughout all regions of space (as in **3** for long distances, R). The cancellation may come about in a variety of ways. It may be forced by symmetry as in *trans*-(0,90)-tetramethylene. Alternatively, it may result from

"accidental" nodal properties that have nothing to do with symmetry, as in the through-space interactions in **9**. Finally, the cancellation may be caused by a precise balancing of through-bond and through-space interactions (**1**, **4**, and **6**).

Closs' biradical (**1**) falls into the third category and is thus a triplet due to a fortuitous balance of through-bond and through-space effects. The results of the present work would seem to significantly restrict the class of biradicals that will be observable under the conditions of the Closs experiment. Prime candidates still include **6** and related trimethylene derivatives.

In another connection, Doubleday has recently speculated that for localized (1,n) biradicals derived from Norrish type I cleavage of cycloalkanones, the number of intervening σ bonds may influence ΔE_{S-T}.[12] While we have not studied any structures that are directly relevant to Doubleday's work, our results do support the general notion since the effectiveness of through-bond coupling should depend upon the number of intervening bonds. Note that for extended conformations of such structures, which would have very small through-space effects, through-bond interactions can only act to favor a singlet ground state.

Communications to the Editor

Substituent Effects on Tin-119 Chemical Shifts in 4-Substituted Bicyclo[2.2.2]octyl- and Bicyclo[2.2.1]heptyl-1-trimethylstannanes

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Tin-119 NMR chemical shifts are very reponsive to structural changes and hence can provide valuable insights into organotin structures, reactions, etc.[1-3] Despite this sensitivity, the direction of any chemical shift response to a tactical structural change is a priori difficult to predict, and in general the understanding of heavy-metal chemical shifts is poor.[4] In a previous study,[5] we

observed that remote 6- and 7-substituents in 1-(trimethylstannyl)-4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalenes (system **1**), in which direct π-type transmission mechanisms are

1   **2**, Y = Sn(CH₃)₃   **3**, Y = Sn(CH₃)₃
          4, Y = F   **5**, Y = F

prohibited, had a surprisingly large influence on the ¹¹⁹Sn chemical shift, and we undertook to examine simpler rigid systems, so that field, through-bond, and other mechanisms for substituent–probe interactions could be assessed for the ¹¹⁹Sn nucleus. A range of 4-substituted bicyclo[2.2.2]octyl- and bicyclo[2.2.1]heptyl-stannanes of types **2** and **3** have now been characterized,[6] and we

(1) Smith, P. J.; Smith, L. *Inorg. Chim. Acta Rev.* **1973**, *7*, 11.
(2) Kennedy, J. D.; McFarlane, W. C. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1975**, *1*, 235.
(3) For a useful review, see: Pereyre, M.; Quintard, J. P.; Rahm, A. *Pure Appl. Chem.* **1982**, *54*, 29.

(4) Smith, P. J.; Tupciankas, A. P. *Ann. Rep. NMR Spectrosc.* **1978**, *8*, 291.
(5) Kitching, W.; Drew, G. M.; Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1981**, *46*, 2252 and references therein.
(6) New compounds have been characterized by ¹H, ¹³C and ¹¹⁹Sn NMR and mass spectra and elemental analyses (C, H). All compounds have been prepared by treating the appropriate 4-substituted bicyclo[2.2.2]oct-1-yl iodides with (trimethyltin)lithium in tetrahydrofuran in the standard way. A full description of these syntheses will be presented later in a main writeup.