PHYSICAL AND THEORETICAL STUDIES OF

LOCALIZED ORGANIC BIRADICALS

Thesis by

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When I first announced my decision to leave Caltech (to pursue a
degree in law), one person responded, ''Boy, you must have really
hated it around this place''. Initially, I was surprised by the
comment, but it gradually occured to me that other people were
probably coming to the same conclusion. At last I have a chance to
set the record straight. Don't worry — I'm not going to say that the
last two years have been the best of my life. I've never been a
convincing liar (even on paper) and besides, it's doubtful that anyone
reading this would be stupid enough to believe me. Still, the truth
is that the past two years have been two very good ones, and to a
large extent, I have the people at Caltech to thank for that.

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candidacy report and finally to Master's Thesis.

ABSTRACTS

Section I. Introduction

Section II. Singlet-triplet energy gaps in localized

1,3-biradicals have been investigated using _ab initio_ electronic

structure theory. Analysis of both the molecular orbital and

generalized valence bond wavefunctions 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.

Section III. Several unsuccessful attempts to observe the

triplet cyclobutane- and cyclohexane-1,3-diyls through low temperature

photolysis of the corresponding azo and azoxy compounds are reported.

The reasons for these failures are considered together with their

implications for the observation of other localized biradicals.

Section IV. Photolysis of either

7-(2,3-diazabicyclo[2.2.1]hept-2-ene) spirocyclopropane or

7-(2,3-diazabicyclo[2.2.1]hept-2-ene) spiro-5'-bicyclo[2.1.0]pentane

in a glassy matrix at $8^{\circ}K$ leads to observation of a triplet ESR

spectrum. Both signals exhibit zero-field splitting parameters which

are typical of delocalized systems ($|D/hc| = 0.0255$ and $|E/hc| = 0.003$

cm^{-1}). In addition, they are stable at temperatures well in excess of 85°K. Several possible sources of the two spectra are discussed.

Section V. A program for the _ab_ _initio_ calculation of zero-field splitting parameters in localized biradicals is developed. The results for several 1,3-biradicals are presented.

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Section I

Introduction

I. Introduction

Localized biradicals,[1] unlike their more stable counterparts, delocalized biradicals, are usually not isolated or detected by spectroscopic methods but rather are assumed intermediates on the basis of a substantial body of chemical evidence.[2] ESR observation of the first such species, cyclopentadiyl (1), was reported by Closs in 1975.[3] Closs' result promised to remove simple localized biradicals from the realm of ''permissible intermediate'' and ''theoretical model'' to that of thermodynamically and kinetically characterized reactive intermediate. Unfortunately, extension of the experiment to other fundamental localized biradical systems has thus far not proved possible.

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In the current work the reason for this failure is elucidated. First it is shown that only a small number of localized biradicals should exhibit a triplet ground state -- an important requirement for ESR observation of such species (Section II). It is then demonstrated that only a small fraction of even these few biradicals will be observable under the conditions of the Closs experiment. In several instances, the precursor molecules lack the proper photochemistry, while in others, the biradicals may be too flexible to permit an extended lifetime (Section III).

Even though it seems unlikely that many other localized biradicals will ever be observed by ESR, studies on the one fundamental system which _can_ be observed in this manner may still provide useful information about such species. In Sections IV and V, two systems which are structurally similar to, but chemically quite different from **1** are investigated. This work takes advantage of both experimental and theoretical methods.

References and Notes

1. The term ''localized'' is used here in a classical sense, implying that the radical centers are not part of a conventional π-system. However, a major point of this work is that the radical centers do delocalize via the CH_2 groups.

2. (a) Berson, J.A. In ''Rearrangements in Ground and Excited States, Vol. I''; de Mayo, P., Ed.; Academic Press: New York, 1980; 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, Vol. III''; de Mayo, P., Ed.; Academic Press, New York, 1980; pp. 381–444.

3. Buchwalter, S.L.; Closs, G.L. <u>J. Am. Chem. Soc.</u> **1979**, <u>101</u>, 4688–4694.

Section II

Effects of Through-bond and Through-space

Interactions on Singlet-Tripet Energy Gaps

in Localized Biradicals

II. 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 using _ab_ _initio_ electronic structure theory. Analysis of both the molecular orbital and generalized valence bond wavefunctions 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.

Introduction

Biradicals have long been postulated as intermediates in a variety of thermal and photochemical reactions.[1] More recently, direct observation 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-cyclopentadiyl (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 which make the observation of 1 successful would be useful.[7]

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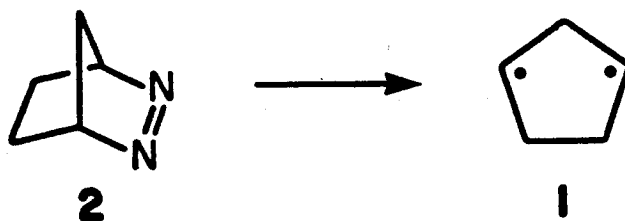
Several lines of experimental evidence[3] and theoretical calculation,[8] indicate that 1 has a triplet ground state. It seems certain that this is a major factor which facilitates its direct observation by ESR. Direct observation of the singlet state of a localized biradical has not yet been accomplished, and in most cases

the lifetimes of such species must be quite short. If a biradical has a triplet ground state, however, the spin forbiddeness 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] 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 using laser flash photolysis techniques[11] and indirectly by CIDNP.[12] Clearly, knowledge of the factors which 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) wavefunctions[14]

for such structures. The GVB approach provides a simple, alternative

model for the following 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 using a valence double-zeta 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 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

wavefunction 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/mole.[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 semi-quantitatively 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 which 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 anti-bonding ($\pi^*_{CH_2}$) -- which 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 wavefunctions for the triplet and singlet states. In the high-spin species, the two electrons must occupy different orbitals, resulting in a simple, single-determinant wavefunction (1). Only for such a wavefunction does the term ''orbital energy'' have its usual meaning, and subsequent discussions of S-A energy gaps will always refer to triplet wavefunctions. 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 wavefuntion (2).[18] The orbitals for this state must 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 wavefunction is determined, for the most part, by the orbital energies. The configuration 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.

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

$$^{1}\psi_{MCSCF} = (c_1{}^2 + c_2{}^2)^{-1/2} \ (c_1 \phi_S\phi_S - c_2 \phi_A\phi_A) \ (\alpha\beta - \beta\alpha) \qquad (2)$$

$$c_1, \ c_2 > 0$$

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 repulsion 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 Fig. 1. At all separations, R, the radical pairs assume a singlet ground state. Evidently, the S-A gap dominates over the exchange repulsions 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/mole.

Figure 1. Singlet-triplet energy gap as a function of internuclear separation, R, for two weakly interacting methyl radicals (3).

3
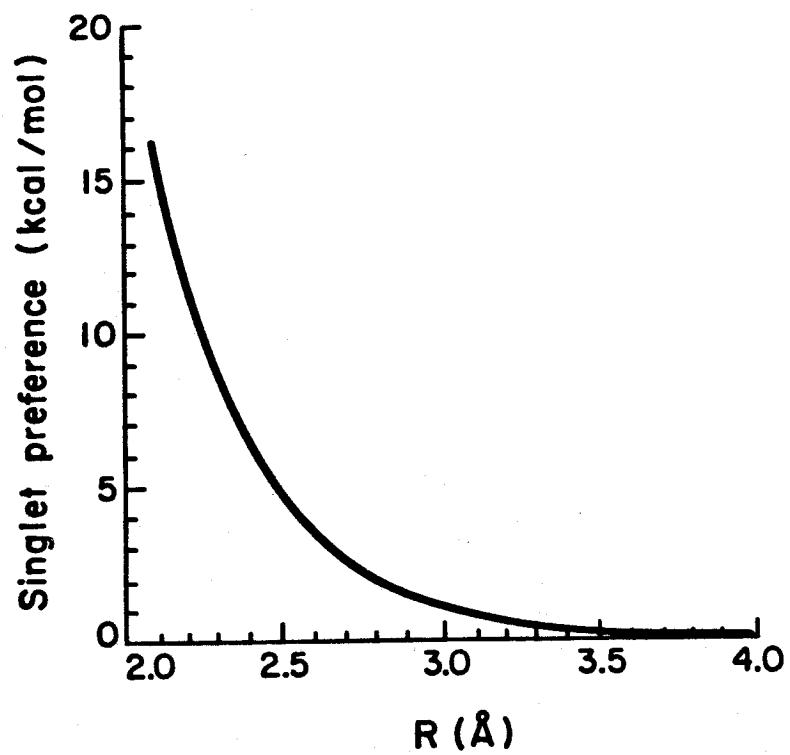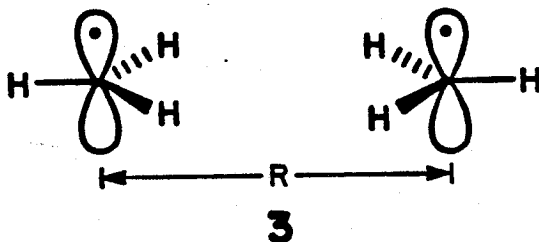
A useful, alternative analysis of such interactions is provided by GVB theory, in which the radical electrons are confined to different orbitals which are optimized self-consistently.[14] The resulting GVB orbitals tend to localize on separate centers so that electron repulsions can be minimized. At 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 Fig. 2.

Singlet and triplet pairing of the GVB orbitals leads to wavefunctions (3) and (4), respectively. It can easily be shown that the singlet GVB wavefunction is equivalent to the MCSCF wavefunction (2), where the GVB orbitals are related to the natural orbitals by Eq. 5. The GVB pair overlap ($S_{\ell r}$) is given by Eq. 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 C_2 (which no longer represent CI coefficients) equal to 0.5. Notice that in this case, the overlap between the orbitals ($S_{\ell r}$) is zero (Eq. 6).

$$^1\psi_{GVB} = (2+2S^2_{\ell r})^{-1/2} (\phi_\ell \phi_r + \phi_r \phi_\ell)(\alpha\beta-\beta\alpha) \quad (3)$$

$$^3\psi_{GVB} = (2-2S^2_{\ell r})^{-1/2} (\phi_\ell \phi_r - \phi_r \phi_\ell)(\alpha\alpha) \quad (4)$$

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.

TWO METHYL RADICALS // R = 2.37

GVB PAIR // OVERLAP = 2.0626D-01
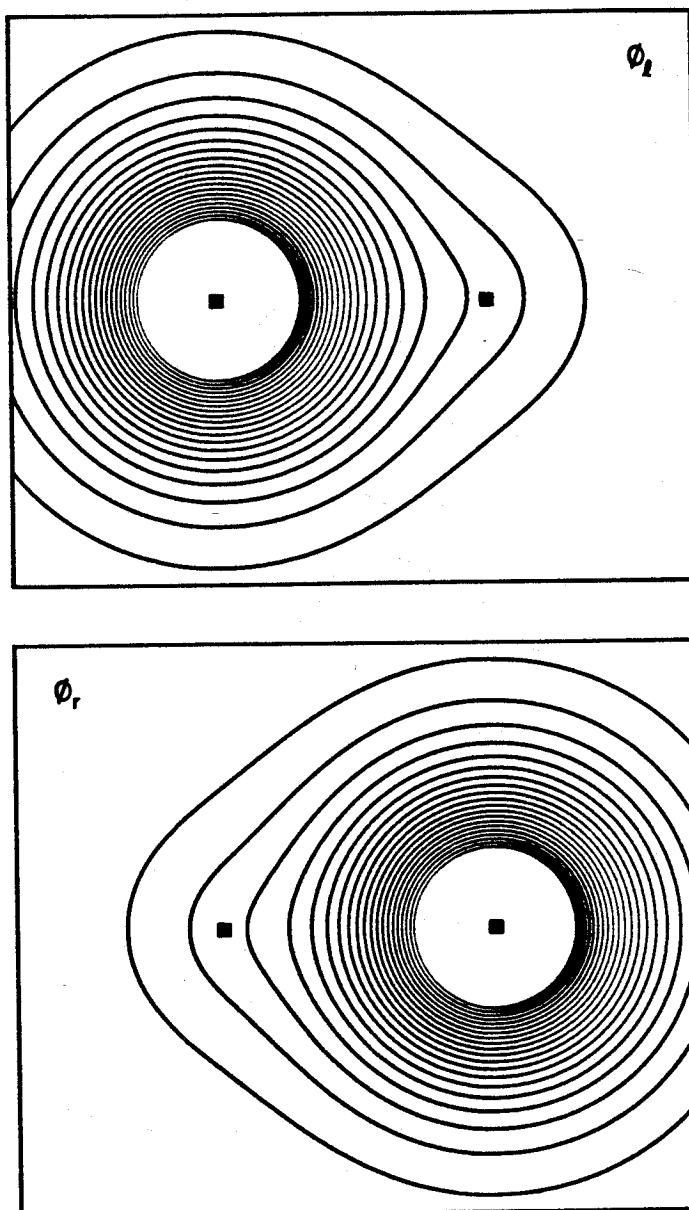
$$\phi_{\ell} = (C_1^{1/2} \phi_S + C_2^{1/2} \phi_A) / (C_1 + C_2)^{1/2} \qquad (5)$$

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

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

$$\Delta E_{S-T} = E_{GVB}^1 - E_{GVB}^3 =$$

$$\frac{4 S_{\ell r} \, h_{\ell r} - 2 S^2_{\ell r} h_{\ell \ell} - 2 S^2_{\ell r} h_{rr} - 2 S^2_{\ell r} J_{\ell r} + 2 K_{\ell r}}{1 - S^4_{\ell r}} \qquad (7)$$

While Eq. 4 is the true high-spin GVB wavefunction, 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 wavefunction involving the same set of orbitals, and this constitutes a major advantage of the GVB analysis of such wavefunctions. It also leads to a simple expression for ΔE_{S-T} (Eq. 7),[24] where h, J, and K are, respectively, 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 $S_{\ell r}$. Taken together, these terms are negative, so that increasing the overlap of the GVB pair favors' the singlet. The fifth term, $2K_{\ell r}$, 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

at short distances and a singlet ground state results. Increasing R

decreases both $S_{\rho r}$ and $K_{\rho r}$. Apparently, $S_{\rho r}$ 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 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.

4
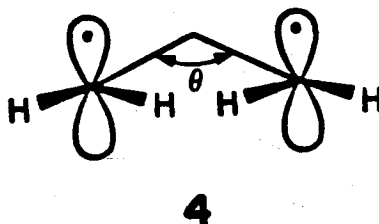
Figure 3 demonstrates that ΔE_{S-T} in 4 is strongly dependent on θ.

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

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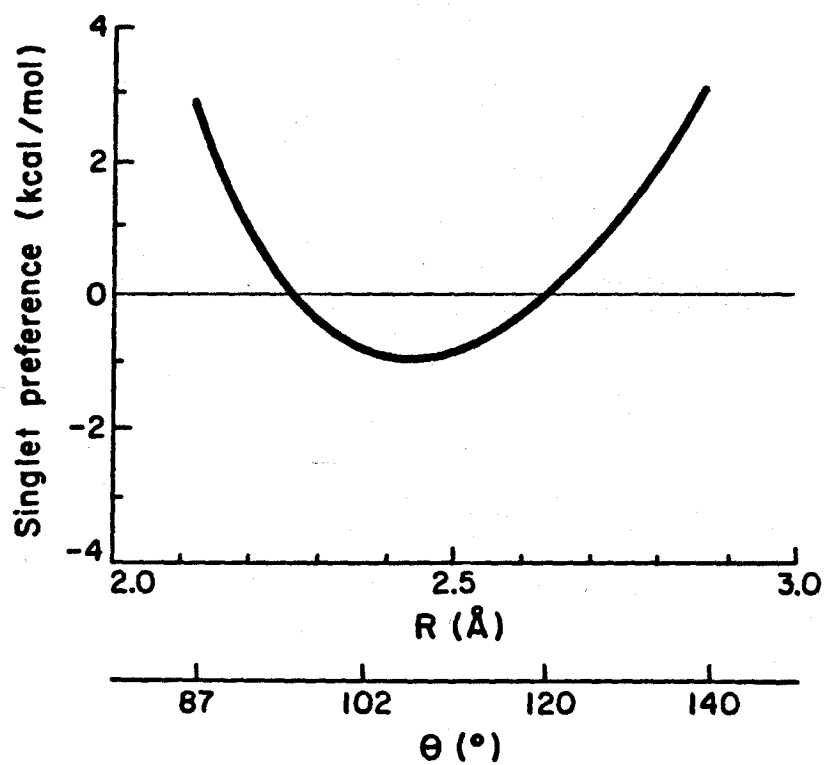
Table I. S–A Gaps and GVB Overlaps for **3** and **4**

| R(Å) | θ(°)[a] | S–A Gap (hartree) | | | S_fr | | |
		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** which leads to the value of R shown. [b]A positive value indicates S below A. [c]Value for **3** minus the value for **4**.

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 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 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]
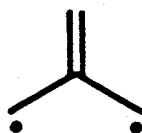
5

In GVB terms, when a through-bond coupling unit is introduced

into a system, both ϕ_ρ 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 (Fig. 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 (Fig. 4a). However, when θ is large, the

second effect is more important, and the radical centers are out of

phase in each GVB orbital (Fig. 4c). Thus, the position of the nodal

surface changes in response to the variation in θ. At intermediate

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.
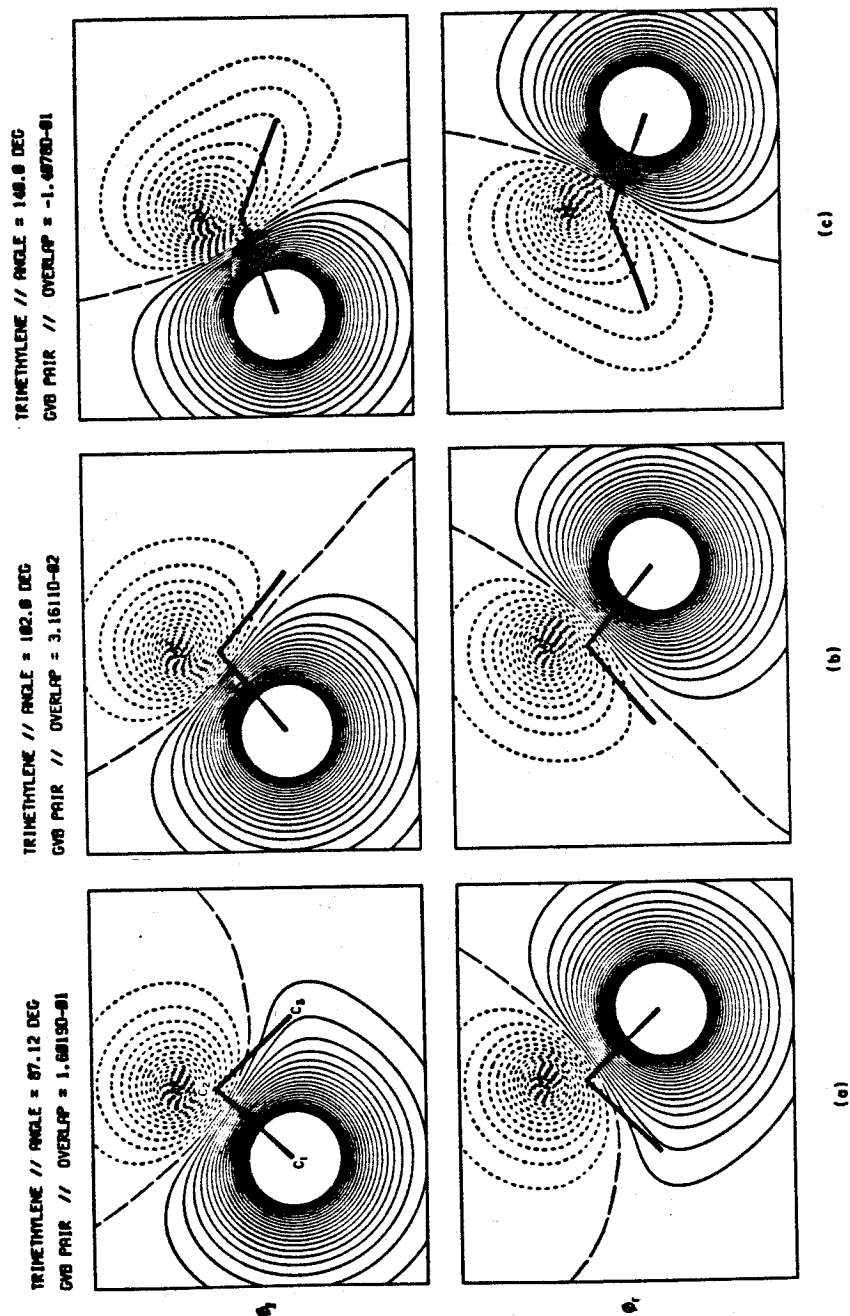
values, the node passes almost directly through the ''far'' center
(Fig. 4b).

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 (Fig. 4), the
contribution to the overlap of the GVB pair ($S_{\ell r}$) 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 (Fig. 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 through-bond coupling unit. The overall
magnitude of $S_{\ell r}$ is thus diminished and eventually $S_{\ell r}$ 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 $S_{\ell r}$ (Fig. 4c). The sign of the overlap, of course, has no
true physical meaning. Thus, one is left with the counter-intuitive
result that increasing the distance between the radical centers can
actually increase the GVB pair overlap.

The quantitative trend in $S_{\ell r}$ with varying θ is shown in Table I.
At all values of θ, $S_{\ell r}$ 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 $S\rho_r$ 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 $\theta = 87^\circ$ or 140° (Fig. 3). At intermediate angles, $S\rho_r$ approaches, and ultimately reaches zero. However, $K\rho_r$ does not go to zero like it did in the through-space model system (3). This is because, when $S\rho_r$ is diminished by special nodal properties of the GVB orbitals (as it is with through-bond coupling), the $1/r$ term in K_{ρ_r} necessarily leads to a finite positive value for the integral.[29] A triplet ground state thus results.

The similarity of the roles of $S\rho_r$ 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 wavefunction cause $S\rho_r$ 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. $S\rho_r$ 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 ($S_{\rho_r} \approx 0$), 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-cyclobutadiyl (**6**), we have recently photolyzed azoalkane **7**[31] at

8°K in a variety of matrices. However, we have been unable 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 1···3 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 ($S_{\rho_r}=0.004$).

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''.

7   **6**
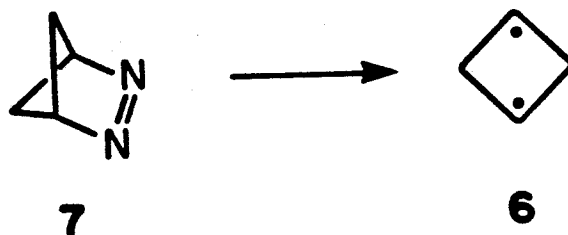
It is interesting in the present context to examine the inorganic

biradical ozone (**8**), which is isoelectronic with **4**. For a given

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 $S\rho_r$. Since

the system starts with only a very small overlap and the through-bond

coupling is quite effective, the final absolute value of $S\rho_r$ is large.

Ozone thus has a strong preference for singlet spin multiplicity.[14,35]
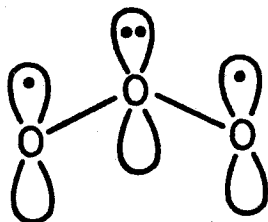
8

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)-tetramethylene (9).[19,36] It should be clear that similar reasoning can be applied to other systems.
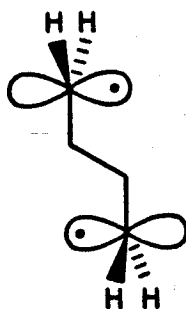
9

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 ($S_{\ell r}=0.003$). 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 the radical separation by moving one p-orbital along its axis yields an overlap

which is <u>larger</u> in magnitude. The reason for this apparent paradox

can be seen in structures **10–12**. In **10**, two p-orbital 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 $S\ell_r$, just as they did for the nearly orthogonal GVB

orbitals of trimethylene with $\theta=102^\circ$. 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 $K\ell_r$ 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.
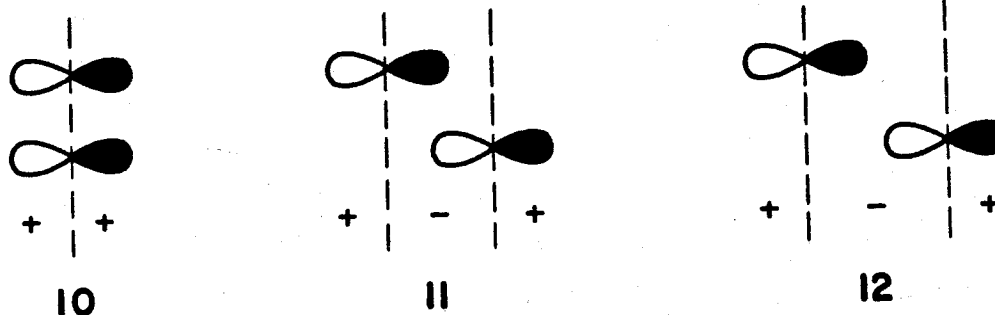
Introduction of the C2-C3 bond as a through-bond coupling unit in 9 once again causes each GVB orbital to incorporate that element in an antibonding way (Fig. 5). This induces a small contribution from the ''far'' centers, which are included in such a way as to minimize one-electron energies. Since there is no significant through-space overlap, the net result can only be an increase $|S_{\rho_r}|$. It is worth noting that the sign of the overlap between the orbitals (S_{ρ_r}), 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.

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.

TETRAMETHYLENE
GVB PAIR // OVERLAP = 7.5891D-02
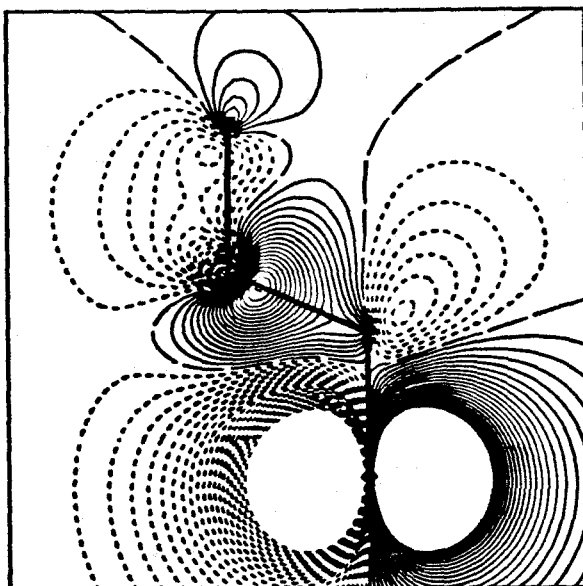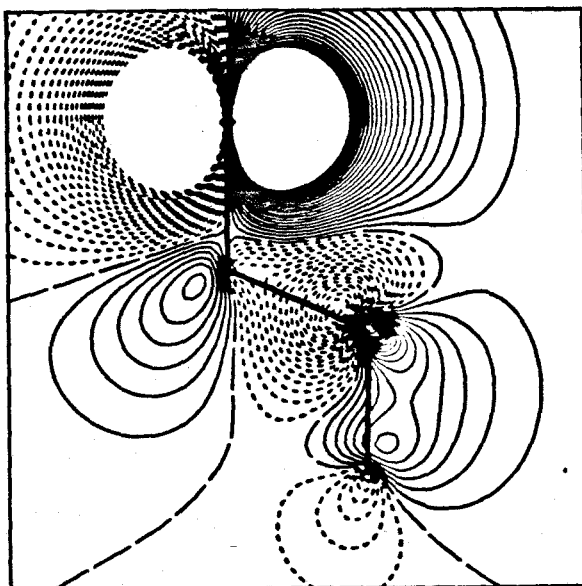
Conclusion

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 $|S_{\rho r}|$ must be significantly smaller than $K_{\rho r}$ This can only be accomplished when $S_{\rho r}$ 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 which have nothing to do with symmetry, as in the through-space interaction 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 which 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 which 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.

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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. See Section III.

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

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and it is quite possible that in some cases the photochemistry

of the biradical precursor undermines the experiment (see below).

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19. Borden, W.T.; Davidson, E.R. J. Am. Chem. Soc. **1980**,

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22. Overlap appears to be the factor most responsible for favoring

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23. The C-H bond lengths in the two methyl radicals were chosen

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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,

equation 7 very closely approximates ΔE_{S-T}.

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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**, <u>96</u>, 3754-3758 and Davis,

   J.H.; Goddard, W.A., III Ibid. **1977**, <u>99</u>, 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.

29. As shown below, the exchange integral, K_{fr}, depends explicitly

   on the overlap <u>function</u> (f), as opposed to the overlap

   integral, S_{fr}, which is the integral of f over all space.

$$K_{fr} = \iint \phi_f(1)\phi_r(1) \cdot (1/r_{12}) \cdot \phi_f(2)\phi_r(2)\, d\tau_1 d\tau_2$$

$$= \iint f(1) \cdot (1/r_{12}) \cdot f(2)\, d\tau_1 d\tau_2$$

At intermediate geometries of (0,0)-trimethylene, even though S_{fr}

approaches zero, f does not. The integrand of K_{fr} 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, $K_{\rho r}$ will be positive even when $S_{\rho r}$ is zero.

30. Dixon, D.A.; Dunning, T.H., Jr.; Eades, R.A.; Kleier, D.A. J. Am. Chem. Soc. **1981**, 103, 2878-2880.

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32. The geometry of the carbon framework was assumed to be identical to 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-zeta 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.

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

Section III

Attempted Observation of the Cyclobutane-

and Cyclohexane-1,3-Diyls

III. Attempted Observation of the Cyclobutane-
and Cyclohexane-1,3-Diyls.

Introduction

The calculations in Section II show that at least part of the
reason Closs' experiment[1] on the cyclopentane-diyl has not been
extended to other localized biradical systems is that only a small
fraction of these species exhibit the sensitive balancing of
through-bond and through-space effects which is necessary to produce a
triplet ground state. Nevertheless, one still might expect most
simple 1,3-diyls to be observable by ESR. Unfortunately, the azo
precursors to these biradicals have generally been synthetically
inaccessible.

Over the last few years, this obstacle has been rapidly overcome.
In 1980, Wilson[2] published a general synthesis for bicyclo[n.2.1] azo
compounds with $n \geq 2$. More recently, Chang of this laboratory reported
a method for making the remaining member of the series, with n=1 (1).[3]

1   2
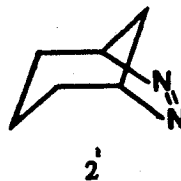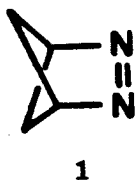
The present work was therefore undertaken to determine whether
photolysis of any of these newly-available azo compounds might lead to
ESR observation of the corresponding 1,3-diyls. The systems chosen
for initial study were 1 and 2.

Results and Discussion

2,3-Diazabicyclo[2.1.1]hex-2-ene (1). When **1** is irradiated in a matrix at 8°K, a single, intense ESR peak is observed. It is believed that this signal arises from mono-radicals which are formed as azo-derived biradicals abstract hydrogen atoms from adjacent solvent molecules. Unfortunately, the broad nature of the hyperfine splittings precludes any more detailed analysis.

3

Of course, the absence of triplet resonances in the spectrum does not necessarily mean that **3** has a singlet ground state. More probably, it simply indicates that **1** is an unsuitable photochemical precursor for the triplet biradical. Chang[3,4] has shown that the triplet azo compound does not lose nitrogen, but undergoes β-cleavage to **4**, instead (Scheme I). This rearrangement product, in fact, is the major product of photolysis at low temperature. The singlet azo compound, in contrast, does lose nitrogen. However, the resulting singlet biradical apparently closes before it has a chance to intersystem cross to the presumably lower-lying triplet.

Scheme I
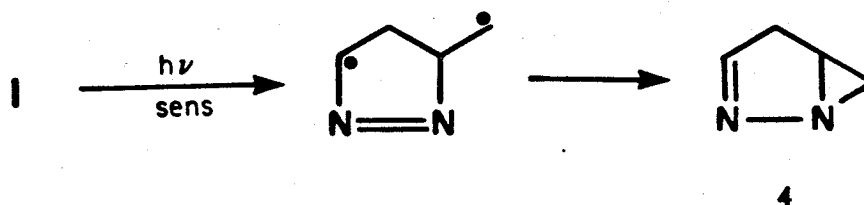
2,3-Diazabicyclo[2.1.1]hex-2-ene N-oxide (5). In order to circumvent the unfortunate photochemistry of 1, an attempt was made to generate 3 through photolysis of the azoxy compound, 5. Previous studies by Michl[5] suggested that the major photoproduct of 5 would be the oxadiaziridine compound, 6. It was hoped, however, that a small amount of the compound would also lose N_2O to give 3. Evidently this did not happen. A triplet signal could not be observed upon either direct or triplet-sensitized photolysis of 5. Moreover, analysis of the reaction mixtures provided no evidence of decomposition.
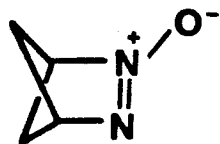
5
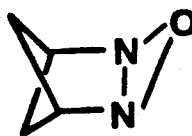
6

2,3-Diazabicyclo[3.2.1]oct-2-ene (2). Photolysis of **2** at 8°K in the ESR cavity failed to give either a triplet or a doublet signal. The azo compound did undergo decomposition, however. Analysis of the reaction mixtures revealed a total of three products: cyclohexane, cyclohexene, and a final one, which is believed to be bicyclohexane (**7**).[6]

The reason for the absence of any ESR signals is unclear, especially since the photochemistry of **2** has never been studied in detail. However, assuming the biradical **8** is formed, one might reasonably expect observation of this species to be complicated by its high degree of flexibility. Certain distortions of the biradical, for example, might facilitate closure to **7** by placing the radical orbitals in a conformation more conducive to intersystem crossing.[7] Furthermore, it is possible that the optimum biradical geometry might differ enough from the idealized (0,0)-trimethylene-like geometry to result in a singlet ground state for the system.
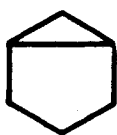
7   8

Conclusion

It is now possible to appreciate how remarkable Closs'
observation of the cyclopentane-diyl truly was. The calculations in
Section II demonstrate that only a limited class of localized
biradicals should exhibit a triplet ground state -- an important
requirement for ESR observation of such species. The current work
further shows that not all of even these few biradicals will be
observable under the conditions of the Closs experiment. The
precursor molecules must have the proper photochemistry (as **1** does
not) and the biradicals may have to be somewhat rigid (as **8** apparently
is not).

Experimental

**2,3-Diazabicyclo[2.1.1]hex-2-ene (1) and
2,3-Diazabicyclo[2.1.1]hex-2-ene N-oxide (5).** These compounds were
graciously provided by Moon Ho Chang of this laboratory.[3]

2,3-Diazabicyclo[3.2.1]oct-2-ene (2). This azo compound was
synthesized by a modification of the literature procedures.[2,8] First,
crude 5-hexenaltosylhydrazone was prepared in two steps from
5-hexen-1-ol (Pfaltz and Bauer), as described by Wilson.[2] The white
solid was then dried for 12 hours under high vacuum before being used
in the subsequent cyclization.

A 4.0 gm sample of crude tosylhydrazone was dissolved in 100 ml
of dry CH_2Cl_2, and the solution cooled to 0°C under nitrogen. Upon

addition, by syringe, of 2.4 ml $BF_3 \cdot Et_2O$ the mixture turned milky

yellow in appearance. The solution was stirred for 4 hr. at $0^\circ C$ and

48 hr. at room temperature, after which time the mixture was extracted

(3x75 ml) with saturated sodium bicarbonate. The combined aqueous

washings were extracted further with CH_2Cl_2 (2x75 ml), and the

combined organic extracts dried over $MgSO_4$. Removal of the solvent

left a brownish-yellow paste which was purified by Kugelrohr

distillation at $90^\circ C$ and 0.01 torr. Separation of the azo compound

from unreacted starting material was incomplete and accompanied by

some decomposition, but yielded approximately 100 mg of 99.95% pure

material.

Preparation of ESR Samples. Samples were prepared by dissolving

the compound to be studied in enough purified solvent to make a 0.1 M

solution. For the sensitization experiments, 0.25 mole/liter of

either benzophenone or propiophenone was also added. The solutions

were placed in 5 mm o.d. quartz ESR tubes (Wilmad) equipped with high

vacuum stopcocks. The tubes were then degassed through three

freeze-pump-thaw cycles and frozen in liquid nitrogen, before finally

being inserted into the precooled ESR cavity.

ESR Experiments. A Varian E-9 spectrometer was outfitted with

both an Air Products and Chemicals Helitran liquid helium transfer

apparatus and an Oriel 200-W mercury-xenon lamp, which was focused

into the microwave cavity. The output of the lamp, which was

generally operated at 120-150W, was filtered through water, Pyrex,

and, in the sensitization studies, a 365 nm cutoff filter.

The temperature at the sample was checked both periodically, with a calibrated thermocouple sealed in a sample tube, and continuously, with a less accurate thermocouple located 1 cm below the sample in the quartz Dewar. Heating above the minimum temperature (about 8°K) was achieved by adjusting either the helium flow rate or the Helitran automatic temperature controller.

Analysis of Product Mixtures. The product mixtures from **1** were analyzed, after warming, by gas chromatography on a column of 20''x1/8'' 10% UCW 982 on Chrom W, mesh size 80/100. Column temperature was maintained at 40°C and the gas flow kept at 128 cm^3/min. The product mixtures from **2** were similarly analyzed on a column of 72''x1/8'' 5% OV-17 on Chrom P. Column temperature was kept at 50°C for 15 minutes and then increased to 110° at a rate of 20°/min. The gas flow was maintained at a constant 35 cm^3/min.

References and Notes

1. S.L. Buchwalter and G.L. Closs, <u>J. Am. Chem Soc.</u>, <u>101</u>, 4688 (1979).

2. R.M. Wilson, J.W. Rekers, A.B. Packard, and R.C. Elder, <u>J. Am. Chem. Soc.</u>, <u>102</u>, 1633 (1980).

3. M.H. Chang and D.A. Dougherty, <u>J. Org. Chem.</u>, <u>46</u>, 4092 (1981).

4. M.H. Chang and D.A. Dougherty, <u>J. Am. Chem. Soc.</u>, <u>104</u>, 2333 (1982).

5. W.R. Dolbier, J., K. Matsui, H.J. Dewey, D.V. Horak, and J. Michl, <u>J. Am. Chem. Soc.</u>, <u>101</u>, 2136 (1979).

6. Detailed product studies were not performed, in part because the third product could not be easily separated from the cyclohexene. It was observed, however, that cyclohexene and the third product (presumably **7**) were formed in nearly equal amounts. In addition, cyclohexane, only a minor product under conditions of direct photolysis, was the <u>major</u> product in the sensitization experiments.

7. For a review of orbital alignments which are favorable to intersystem crossing, see L. Salem and C. Rowland, <u>Angew. Chem. Int. Ed.</u>, <u>11</u>, 92 (1972).

8. A. Padwa and H. Ku, <u>J. Org. Chem.</u>, <u>45</u>, 3756 (1980).

Section IV

ESR Studies of Spiropentane-based Rearrangements

IV. ESR Studies of Spiropentane-based Rearrangements

Introduction

One of the most intriguing possible fates of a localized biradical is its conversion to another biradical species -- either localized or not. The most studied reaction of this type is probably the spiropentane rearrangement.[1] Thermolysis of spiropentane (1) leads to structural isomerization, as shown in Scheme I.[2] The first step in the reaction is known to be cleavage of a peripheral bond to form the cyclopropyldicarbinyl biradical, **2**.[3] This process is presumably then followed by cleavage of a second bond to form the ''allyl + p'' biradical, **3**,[4] which finally closes to methylenecyclobutane (**4**). The same pathway is apparently involved in the thermal decomposition pyrazoline **5** (Scheme I).[5]

Modification of the spiropentane system by addition of an ethano bridge (**6**) leads to an almost identical sequence of events (Scheme II).[6] Both thermal and photochemical decompositions of **6** generate biradical **7**, which can either close to **8** or rearrange, through biradical **9** to olefin **10**. The ratio of the two products is highly dependent upon the spin state of the first-formed biradical,**7**.[7] In the singlet manifold, closure to **8** is efficient, while in the triplet, closure is forbidden and rearrangement dominates.

Even though addition of a single ethano bridge only marginally alters the chemistry of the spiropentane system, McElwee-White of this laboratory has shown that addition of a _second_ bridge dramatically changes the chemistry.[8] Thermolysis and direct photolysis of **11** both

Scheme I
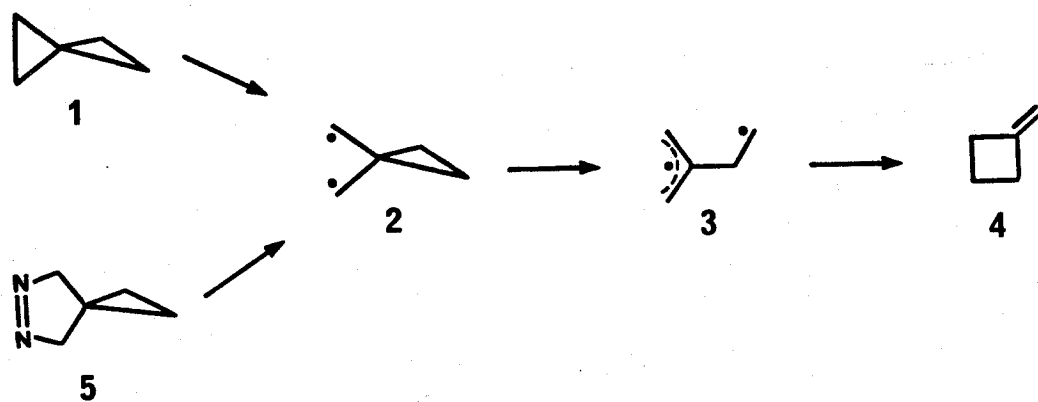
Scheme II
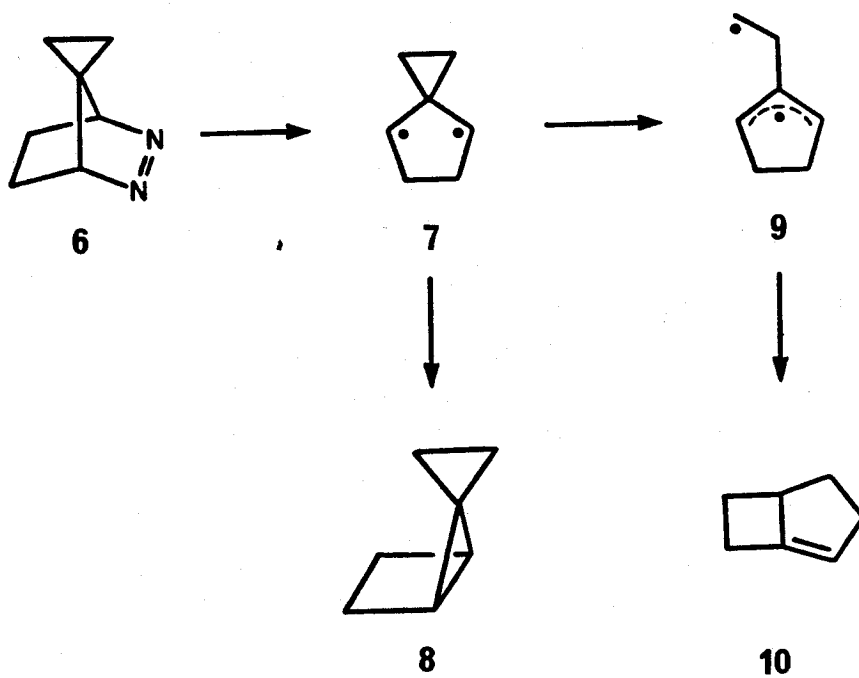
lead to the expected closure product **12**. Triplet sensitized

photolysis of the azo compound, however, yields divinylcyclopentene

(19) as the major product. Deuterium labeling studies show that this

product is formed by at least two, and perhaps as many as three

parallel rearrangements of the first formed biradical, **13** (Scheme

III). The conventional spiropentane rearrangement (path a) is known

to be operative in this system, as is internal radical attack on the

strained bicyclopentane bond (path c).[9] In addition, cleavage of the

bicyclopentane bond to give the spiroconjugated tetraradical **16**, may

also take place.

11   **12**
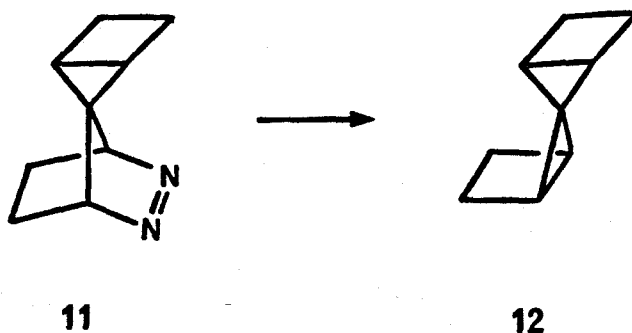
Despite all the interest in these spiropentane-based

rearrangements, remarkably little has been done to study the

intermediate species directly. The present work was undertaken to see

whether any of the triplet biradicals could be observed by ESR.

Positive identification of any of these species would, by itself, be

an important finding, and identification of more than one might permit

a direct study of the interconversion between biradicals.

Scheme III
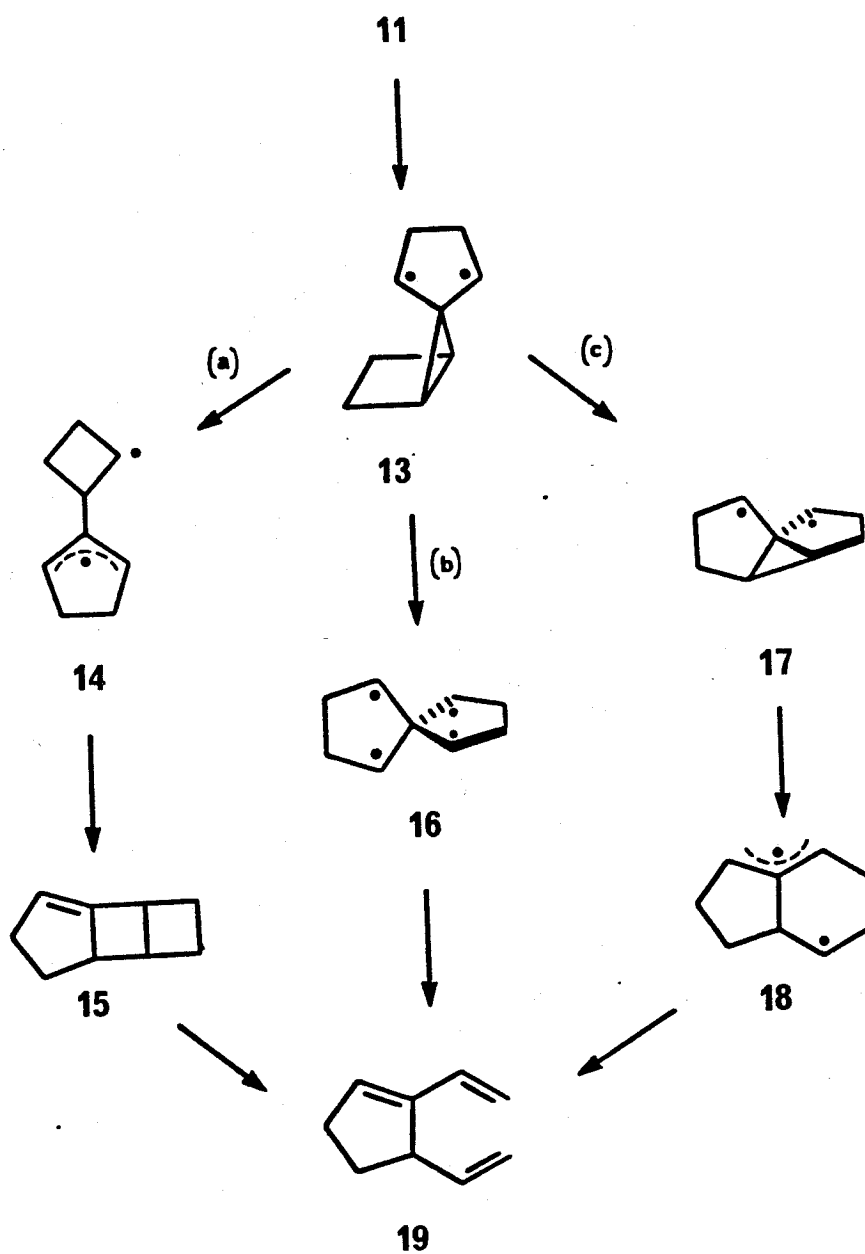
Results and Discussion

Irradiation of **11** in a glassy matrix of 2-methyl

tetrahydrofuran[10] at 8°K leads to observation of the ESR spectrum

shown in Figure 1. The general form of the signal — including the

presence of a half-field, $\Delta m_s = 2$ transition — suggests that it

arises from a single triplet species.[11] The position of the $\Delta m_s = 1$

transitions indicate zero-field splitting parameters of $|D/hc| =$

0.0255 and $|E/hc| = 0.003$ cm^{-1}. Almost identical values are found in

the photolysis of **6**.[12]

In order to identify the source of the two ESR signals, it is

useful to compare the observed zero-field splitting parameters to

those previously found in other organic biradicals. As shown in Table

I, the observed D-values are much smaller than one would normally

expect for a localized biradical such as **20**. While this fact would

seem to rule out the structurally related species, **7** and **13**, as

sources of the observed signals, it is possible that the cyclopropane

ring in these compounds could allow the radical orbitals to delocalize

enough to account for the lower values.

The extent to which this type of delocalization occurs has

already been extensively studied by Roth.[6] He has shown that the

bridge flip barrier in **21** is only 10 kcal/mole smaller than that in **22**

— a difference which is easily explained in terms of the release of

spiro strain in **21** which is not present in **22**. For this reason it

appears that there is no special electronic interaction between the

cyclopropane ring and the radical orbitals. This conclusion is also

supported by _ab initio_ calculations of the zero-field splitting

Figure 1. ESR spectrum obtained upon irradiation of a 2-methyl tetrahydrofuran matrix containing 11 at 8°K.
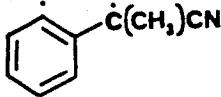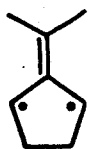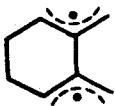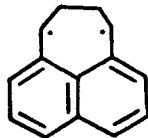
(a) Full Field spectrum
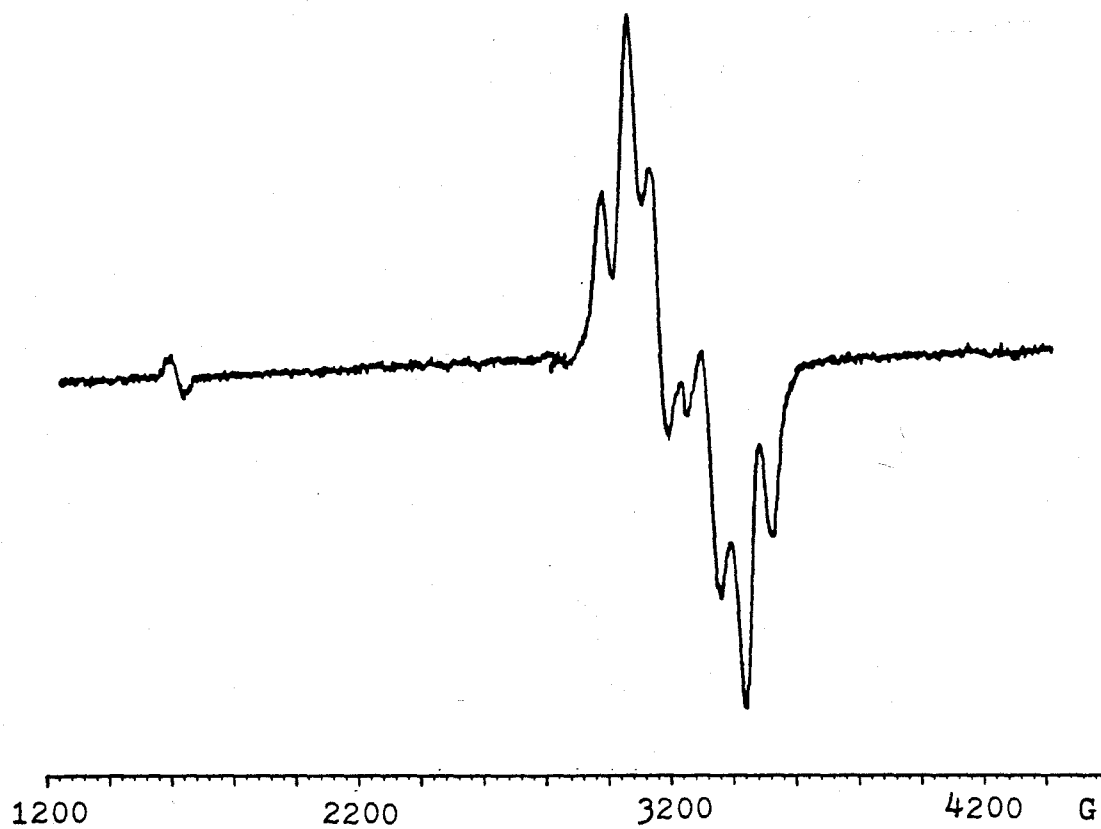
(b) Hyperfine structure on the $\Delta m_s = 2$ peak

Table I. Zero-field splitting parameters for various biradicals [16]

Biradical	$|D/hc|$ (cm^{-1})	$|E/hc|$ (cm^{-1})
	0.024	0
	0.1069	0.0058
	0.027	0.0023
	0.0204	0.0016
	0.018	0.003
	0.084	0.0020

parameters. Even though introduction of the spiro-cyclopropane group does cause a noticeable reduction in the predicted D-value,[13] the effect is not large enough to account for the full experimental decline.

20   **21**   **22**
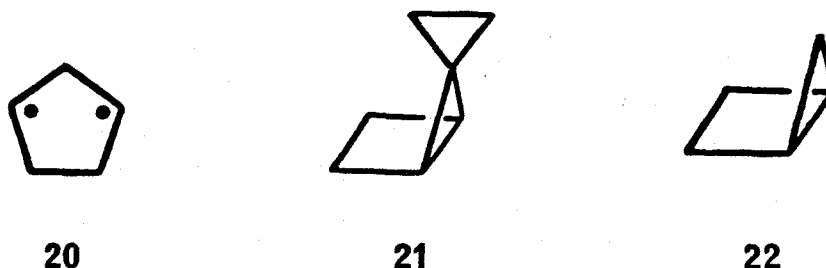
Another factor which militates against 7 and 13 as the currently observed triplet species is the persistence of the two ESR signals at high temperatures. The biradicals generated from both 6 and 11 are indefinitely stable at temperatures in excess of 85°K. In the first case, the biradical is even stable at 146°K.[14] Biradical **20**, in contrast, has only a 15 minute half-life at 8°K.[16] Of course, it is possible that the cyclopropane moiety could perturb the system in such a way as to enhance the stability of the triplet state. For example, one would expect the tunneling reaction which accounts for most of the bicyclopentane (**22**) generated from **20** at low temperatures[16] to cease as the mass of the tunneling species is increased from 14 (for CH_2) to 40 (for cyclopropane) or 66 (for ''housane'').[16,17] Still, this effect cannot explain the full stability of the unidentified triplets. The fact that decay is imperceptible at temperatures as high as 85°K or 146°K suggests that the E_a for closure is at least 5 kcal/mole, and probably greater than 8 kcal/mol[18] — in either case significantly higher than 2.3 kcal/mole barrier reported for closure of **15**.[16] It is

unclear exactly how the cyclopropane or ''housane'' group could cause such a dramatic increase.

While the first-formed biradicals, **7** and **13**, appear to be unlikely sources of the ESR signals, the ''allyl+p'' biradicals that result from rearrangement of these species (**9** and **14**, respectively) seem to be much more viable candidates. Both of these species, for example, exhibit allylic resonance, which could account for the low observed D-values. This resonance (together with any interactions between the non-bonded allyl orbital and the non-conjugated p-orbital) might also help explain the persistence of the signals at high temperatures.

Other lines of reasoning, however, argue against these biradicals as the unidentified triplet species. For example, in order for the ESR signal to appear rapidly at 8°K, the C-C bond cleavage which takes **7** to **9** (or **13** to **14**) would have to be unusually facile.[19] At the same time, the bond formation process that takes **9** to **10** (or **14** to **15**) would have to be extremely slow, so that the signal could persist at high temperatures. This latter requirement seems particularly unattainable in the absence of any steric or orbital-alignment constraints to closure.

Even though the allyl+p biradical is the only triplet species to which **7** can rearrange, there are three alternatives in the case of biradical **13**.[8] One is the spiroconjugated tetraradical **16**. Unfortunately there are two lines of evidence which eliminate this species as a possible source of the ESR signal. First, a Curie plot of signal intensity versus inverse temperature[11] indicates that the observed biradical has a triplet ground state (Fig. 2). This result

Figure 2. Curie plot for the triplet species generated upon
photolysis of **11**. The corresponding plot for
6 has previously been reported.[12]
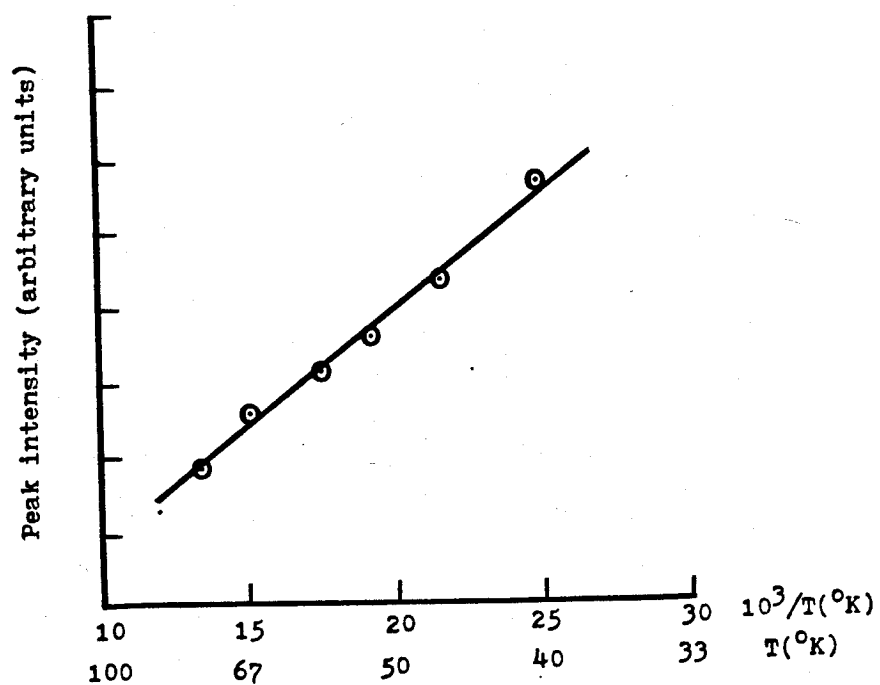
is in direct conflict with MC-SCF calculations which predict a _singlet_ ground state for **16**.[20] Second, the observed E/hc is not consistent with a species of D_{2d} symmetry.[21] Of course, the tetraradical might deviate from this symmetry to relieve the degeneracy of the non-bonding molecular orbitals. However calculations once again show that such a distortion is disfavored.[20]

Another possible rearrangement product from **13** is the localized biradical **17**.[8] This species, however, is also an unlikely carrier of the triplet signal. Calculations of the zero-field splitting parameters using the point charge method[22] suggest that two p-orbitals in the appropriate geometry[23] should give a D-value which is much greater than the one observed (0.108 versus 0.0255 cm^{-1}).[24] Interactions with the cyclopropane ring might work to lessen this difference, but the geometry would seem to preclude any strong interactions.

The only remaining biradical which is known to play a role in the photochemistry and thermochemistry of **11** is another allyl+p biradical, **18**.[8] As with the related species, **9** and **14**, **18** would be expected to exhibit a low D-value and a high degree of thermodynamic stability. In addition **18** has a _kinetically_ stabilizing factor: poor alignment between the radical orbitals and the C-C bond that must break as **18** is converted to **19**. The chief problem with this species as the unidentified biradical is the lack of any corresponding intermediate from the other azo compound (**6**). It seems most reasonable that the two signals should arise from similar species.

The above discussion exhausts the list of biradicals which are currently believed to participate in the ''high'' temperature

chemistry of **6** and **11**. The low temperature chemistry of the compounds, however, may involve still other species. One particularly interesting set of possibilities consists of the trimethylenemethane (TMM) biradicals, **23**, **24** and **25**. These species correspond to the hydrogen shift products of **9**, **14** and **18**, respectively.[25] It is already known that TMM derivatives have zero-field splitting parameters almost identical to the ones currently observed (Table I). In addition, they have triplet ground states and are stable at elevated temperatures,[26] just like the unidentified biradical species. Of course, the TMM biradicals would be expected to lead to other products than **10** and **19**.[26] However, the failure to observe new products at low temperatures does not rule out these species. The ESR technique is so sensitive that even a low level impurity could provide a strong signal.[11]
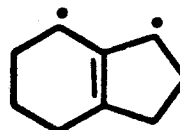
23   **24**   **25**

The extreme sensitivity of the method further raises the specter that untraceable azo impurities might be responsible for the ESR signals. Another conceivable danger is that the signals do not come from biradicals at all, but originate instead from triplet radical pairs that might be generated via biradical abstraction of solvent hydrogens. This seems highly unlikely, however. One would expect the wide distribution of matrix sites to prohibit the kind of extensive hyperfine structure observed on the $\Delta m_s = 2$ peaks (Fig. 1b).

Conclusions

The triplet species which are generated through the photolysis of 6 and 11 remain unidentified. Even though certain intermediates seem more likely candidates than others, none can be completely ruled out. Further experiments will undoubtedly have to be performed to resolve this issue.

Experimental

7-(2,3-diazabicyclo[2.2.1]hept-2-ene)spirocyclopropane (6) and 7-(2,3-diazabicyclo[2.2.1]hept-2-ene)spiro-5'-bicyclo[2.1.0]pentane (11). The two azo compounds, synthesized as reported in the literature,[6,8] were graciously provided by Lisa McElwee-White of this laboratory.

Preparation of ESR Samples. Samples were prepared by dissolving the compound to be studied in enough purified solvent to make a 0.1 M solution. The solutions were placed in 5 mm o.d. quartz ESR tubes (Wilmad) equipped with high vacuum stopcocks. The tubes were then degassed through three freeze-pump-thaw cycles and frozen in liquid nitrogen, before finally being inserted into the precooled ESR cavity.

ESR Experiments. A Varian E-9 spectrometer was outfitted with both an Air Products and Chemicals Helitran liquid helium transfer apparatus and an Oriel 200-W mercury-xenon lamp, which was focused into the microwave cavity. The output of the lamp, which was generally operated at 120-150 W, was filtered through water and Pyrex.

Before each experiment, the temperature at the sample was checked with a calibrated thermocouple sealed in a sample tube. The temperature was then monitored throughout the experiment with a less accurate thermocouple fixed 1 cm below the sample in the quartz Dewar. Heating above the minimum temperature (about $8^\circ K$) was achieved by adjusting either the helium flow rate or the Helitran automatic temperature controller.

Analysis of Product Mixtures. The product mixtures were analyzed, after warming, by gas chromatography on a column of 20'' x 1/8'' 10% UCW 982 on Chrom W, mesh size 80/100. The gas flow rate was maintained at 50 cm^3/min and the column temperature increased from $60^\circ C$ to $200^\circ C$ at 10°/min.

References

1. For a recent review, see J.A. Berson,''Hypothetical Biradical Pathways in Thermal Unimolecular Rearrangements'' in ''Rearrangements in Ground and Excited States, Vol. I,'' P. de Mayo, ed. (New York: Academic Press, 1980).

2. M.C. Flowers and H.M. Frey, J. Chem. Soc. 5550 (1961); M.C. Flowers and A.R. Gibbons, J. Chem. Soc. B. 612 (1971).

3. J.J. Gajewski, J. Am. Chem. Soc., 92, 3688 (1970); J.J. Gajewski and L.T. Burka, ibid., 94, 8857 (1972).

4. The same ''allyl+p'' biradical has been invoked in the thermal interconversion of 4,4- and 2,2-dideuteriomethylene-cyclobutane: W. von E. Doering and J.C. Gilbert, Tet. Suppl., 7, 397 (1966).

5. K.K. Shen and R.G. Bergman, J. Am. Chem. Soc., 99, 655 (1977).

6. W.R. Roth and K. Enderer, Liebigs Ann. Chem., 733, 44 (1970).

7. ''First formed'' biradical is meant to imply the first formed hydrocarbon biradical. A diazenyl biradical may, of course, precede such a species.

8. L. McElwee-White and D.A. Dougherty, J. Am. Chem. Soc., in press.

9. Internal radical attack may actually be taking place in two different modes. Backside attack is known to occur, and frontside attack may also participate. In either case, the unlabeled compound gives the same biradical, 17.

10. Other matrices, such as perfluorobenzene and 2-methylpentane:

3-methylpentane 1:1, gave similar spectra, as did a

polycrystalline powder of the azo compound. However, in these

cases the signal was not as strong and was partially obscured

by a large doublet peak.

11. J.E. Wertz and J.R. Bolton, Electron Spin Resonance:

Elementary Theory and Practical Applications (New York:

McGraw-Hill, 1972).

12. D.M. Lokensgard and J.A. Berson, unpublished results.

13. Calculations using the program described in Section V

predict D-values of 0.124 cm^{-1} for 20 and 0.101 cm^{-1}

for 13. The input singly-occupied molecular orbitals were

obtained from Restricted Hartree-Fock (RHF) calculations on

the two biradicals, performed with basis sets of double-zeta

quality. The geometry of the five-membered ring in both

systems was fixed as previously optimized by Schaefer:

M.P. Conrad, R.M. Pitzer, and H.F. Schaefer III, J. Am. Chem.

Soc., 101, 2245 (1979). The geometry of the cyclopropane

ring in 13 was optimized by MNDO. This optimization, as

well as the RHF calculation on 13, was performed by Lisa

McElwee-White:

14. Since glasses composed of 2-methyl tetrahydrofuran permit

diffusion over 85°K, stability of the triplet species at

higher temperatures had to be tested in another solvent —

propylene glycol. Temperatures greater than 146°K were not

used due to both the limitations of the Helitrans apparatus

and the expected softening of the matrix at higher

temperatures.[15] Compound 11 was never photolyzed in

propylene glycol, so its stability at high temperatures is still uncertain.

15. G. Fischer and E. Fischer, _Molecular Photochemistry_, __8__, 279 (1977).

16. S.L. Buchwalter and G.L. Closs, _J. Am. Chem. Soc._, __101__, 4688 (1979).

17. Closs has shown that merely increasing the mass of the tunneling species from 12 (for CH_2) to 14 (CD_2) substantially retards the tunneling reaction.

18. This estimate is based on a pre-exponential factor identical to that observed by Closs (i.e., 10^8 S^{-1}).[16]

19. The Arrhenius parameters for a conventional cyclopropyl-carbinyl to allylcarbinyl rearrangement are log A=12.48 and E_a=5.94 kcal/mole: B. Maillard, D. Forrest, and K.U. Ingold, _J. Am. Chem. Soc._, __98__, 7024 (1976).

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21. E/hc is directly proportional to the energy difference between the ''x'' and ''y'' magnetic substates at zero field.[11] In systems with D_{2d} symmetry, these two substates should be degenerate and E/hc should be zero.

22. For a general discussion of the method, see R. McWeeney, _J. Chem. Phys._ __34__, 339 (1961), or A. Pullman and E. Kochanski, _Int. J. Quant. Chem._, 251 (1967). The program used in these studies was an adaptation of the one developed by D.A. Dougherty and J.A. Berson (unpublished work).

23. The two interacting orbitals were assumed to be unperturbed

from their position in the tetraradical. The geometry of the
tetraradical was taken from reference 19. ^{20}

24. For comparison, the same type of calculation predicted a
D-value for cyclopentane-diyl of 0.138 cm^{-1}, compared with
an experimental value of 0.084 cm^{-1}.

25. It should be pointed out that 1,2-hydrogen shifts have never
been proven to occur in radical species.

26. J.A. Berson, Acct. Chem. Res., 11, 446 (1978).

Section V

Development of a Computer Program for

Calculating Zero-field Splitting Parameters

in Localized Biradicals

V. Development of a Computer Program for
Calculating Zero-field Splitting Parameters
in Localized Biradicals.

Introduction

The zero-field splitting parameters obtained from ESR spectra

serve as a convenient means for recognizing particular triplet

biradicals.[1] Indeed, the identification of new species is frequently

facilitated by the comparison of experimental D- and E-values with the

ones previously observed for other biradicals. Obviously, it would be

quite useful if the same values could be calculated from first

principles.
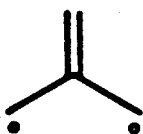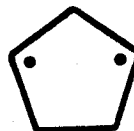
1   2

This problem has generated considerable theoretical interest over

the past 20 years.[2-7] The parameters for delocalized biradicals such

as trimethylenemethane (1) have been calculated several times with

varying degrees of success.[2-7] Unfortunately, one of the major

obstacles in these systems is the inability of a single-determinant

wavefunction to adequately describe the distribution of electron

spin.[2,3] Of course, the same problem would not be as pronounced in

the case of a localized biradical.[8] However, calculations on a

triplet of this type have never been performed.[9] The reason for this

''oversight'' is not difficult to understand; the first localized

biradical was not observed until 1975[10] and this species,

cyclopentadiyl (2), remains the only one seen to date.[11]

The present work was therefore undertaken to develop a program

for calculating the zero-field splitting parameters in localized

biradicals. It was hoped that these efforts would complement the

experimental work described in Sections III and IV. In practice, the

program has proved quite useful in assessing the chances that various

species might be responsible for the ESR signal that is obtained upon

photolysis of 3 and 4.[12]
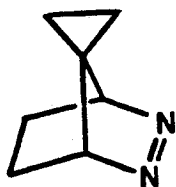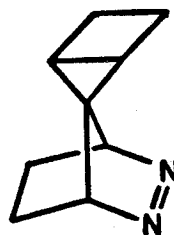
3   4

Overview of Various Possible Approaches

The zero-field splitting parameters of a triplet species are

related to the energies of the three magnetic sublevels at zero

magnetic field. The non-degeneracy of these levels results from

dipole-dipole coupling between the spins of the unpaired electrons.

This interaction can be described in terms of a tensor, D, as shown in

Eq. 1.

$$D = \frac{g^2\beta^2}{2} \begin{bmatrix} \frac{r^2-3x^2}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\ \frac{-3xy}{r^5} & \frac{r^2-3y^2}{r^5} & \frac{-3yz}{r^5} \\ \frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{r^2-3z^2}{r^5} \end{bmatrix} \qquad (1)$$

The elements of D must be averaged over the electronic wavefunction, Ψ, which is simply an antisymmetrized linear combination of the two singly occupied molecular orbitals, ψ_a and ψ_b (Eq. 2). For this reason, the expectation value for each of the operators, $\hat{O}$, can be written as in Eq. 3.

$$\Psi = 2^{-1/2}(\psi_a\psi_b - \psi_b\psi_a) \qquad (2)$$

$$\langle \Psi|\hat{O}|\Psi \rangle = (1/2)\langle(\psi_a\psi_b - \psi_b\psi_a)|\hat{O}|(\psi_a\psi_b - \psi_b\psi_a) \rangle$$
$$= \langle \psi_a\psi_b|\hat{O}|\psi_a\psi_b \rangle - \langle \psi_a\psi_b|\hat{O}|\psi_b\psi_a \rangle \qquad (3)$$

Once Eq. 3 is evaluated for each $\hat{O}$, D may be diagonalized to give ^dD. The diagonal elements of this matrix are the energies of the three magnetic sublevels. The one with the largest absolute value is typically multiplied by a factor of 1.5 to give the scalar zero-field splitting parameter, D. The difference between the other two elements, in contrast, is multiplied by 0.5 to give E.[1]

The problem of calculating D and E thus becomes one of evaluating the integrals in Eq. 3. This can be accomplished in a number of

different ways. First, the integrals may be solved for analytically. This approach has already been employed successfully in the study of delocalized π-systems.[2-4] Unfortunately, most of the formulas needed to compute the integrals in <u>localized</u> systems have not yet been derived.

An alternative method involves the simulation of basis atomic orbitals by a small number of point charges: one for each s-orbital and two for each p-orbital. This technique has proved quite reliable in delocalized systems,[5-7] but it, like the analytical approach, cannot be easily modified for localized biradicals. Calculations show that the D- and E-values predicted for species of this type are strongly dependent on the source of the triplet wavefunction (Table I)[13] — a complication which does not arise in delocalized systems.[14] In addition, the technique cannot properly handle contributions from more than a single orbital on each atomic center. This, of course, is a prerequisite for treating hybrid orbitals and orbitals which do not lie along a coordinate axis.

A final approach is to approximate the two electron distributions (ψ_a and ψ_b) not by a few point charges, but by hundreds or thousands of them. The result is then essentially a numerical evaluation of the integrals. Once again, this method has only been used with delocalized systems in the past.[3]

The Numerical Integration Method

Numerical computation of the integrals in Eq. 3 can be viewed as an approximate method in which the two orbitals, ψ_a and ψ_b, are

Table I. Zero-field splitting parameters calculated for **2** using the point charge method.[13]

Source of Wavefunction	$|D/hc|$	$|E/hc|$
HMO	0.138 cm^{-1}	0.008 cm^{-1}
MNDO	0.056	0.012
RHF	0.067	0.016
UHF	0.070	0.011
[experimental values]	0.084	0.002

expanded in terms of box-like basis functions (Eq. 4). In this scheme, the coefficients of the basis functions correspond to the amplitudes of the orbitals in the appropriate boxes. When the orbital expansions are substituted into Eq. 3, the result is Eq. 5.[15]

$$\psi_a = \sum_i c_{ai}\phi_i \qquad\qquad \psi_b = \sum_j c_{bj}\phi_j \qquad (4)$$

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \sum_i c_{ai}\phi_i \sum_j c_{bj}\phi_j | \hat{O} | \sum_k c_{ak}\phi_k \sum_l c_{bl}\phi_l \rangle$$

$$-\langle \sum_i c_{ai}\phi_i \sum_j c_{bj}\phi_j | \hat{O} | \sum_k c_{bk}\phi_k \sum_l c_{al}\phi_l \rangle \qquad (5)$$

Since the box-like basis functions do not overlap at any point in space, only integrals with i=k and j=l need be considered. Thus Eq. 5 reduces to Eq. 6. For a given i,j pair of basis orbitals, the contribution to the total integral is given by Eq. 7. The term in brackets is a weighting coefficient which depends upon the amplitudes within the boxes, while the integral is a quantity which is determined by the distance between the boxes. Both expressions are easily evaluated, and the various Θ_{ij}'s need only be added together to arrive at the final integral in Eq. 3.

$$\langle \Psi | \hat{O} | \Psi \rangle = \langle \sum_i c_{ai}\phi_i \sum_j c_{bj}\phi_j | \hat{O} | \sum_i c_{ai}\phi_i \sum_j c_{bj}\phi_j \rangle$$

$$- \langle \sum_i c_{ai}\phi_i \sum_j c_{bj}\phi_j | \hat{O} | \sum_i c_{bi}\phi_i \sum_j c_{aj}\phi_j \rangle \qquad (6)$$

$$\theta_{ij} = (C_{ai}C_{bj})^2 \langle \phi_i \phi_j | \hat{0} | \phi_i \phi_j \rangle - (C_{ai}C_{bj}C_{bi}C_{aj}) \langle \phi_i \phi_j | \hat{0} | \phi_i \phi_j \rangle$$

$$= [(C_{ai}C_{bj})^2 - (C_{ai}C_{bj}C_{bi}C_{aj})] \langle \phi_i \phi_j | \hat{0} | \phi_i \phi_j \rangle \qquad (7)$$

Programming Considerations

Each of the integrals in Eq. 3 is a sum over a six-dimensional space (three dimensions for each electron). Consequently, the total number of contributions (θ_{ij}) which must be added together is N^6, where N is the number of boxes in the space along one direction. Of course it is imperative that the number of operations which are actually executed this many times be kept to a minimum. Only in this way can a calculation be limited to a reasonable amount of time.

There are three basic tasks which must be performed in the evaluation of the θ_{ij}'s: 1) computation of the amplitudes within the box-like basis orbitals; 2) evaluation of the weighting coefficients; and 3) calculation of the integrals between boxes. The first of these need only be executed two times within Cartesian space -- once for each orbital -- for a total of $2N^3$ times. The second, however, must be carried out the full N^6 times, since the weighting coefficients depend upon the coordinates of both electrons. Finally, the third operation, calculation of the integrals between boxes, has to be performed once for every unique vector linking two boxes. Several i,j pairs will obviously have the same vector joining them, and it can be shown that the total number of unique vectors is only $(2N-1)^3$.[16]

The figures above represent the number of times that each computation must be carried out in the most general case. In

molecules with symmetry, however, these values can be reduced

substantially. For example, if the amplitudes, weighting

coefficients, or basis set integrals are the same in different regions

of space, only a fraction of these quantities need to be separately

evaluated.[17] Moreover, certain of the D-tensor elements may be forced

to zero, depending upon the type of symmetry present.[18] All of these

factors can be useful in making the calculations of the integrals as

efficient as possible.

Results and Discussion

The two programs developed for calculating zero-field splitting

parameters (one for π-biradicals with C_{2v} symmetry) are shown in the

Appendices, together with a description of the input data and a sample

input deck. The programs satisfy numerous criteria for internal

consistency. For example, the results vary only slightly with changes

in the size and number of the basis-set boxes (Table II). In

addition, the predicted D- and E-values are independent of the

orientation of the molecules.[19] Finally, the normalization integral

(Eq. 3 with O=1) approaches 1.0 as the size of the basis orbitals is

reduced (Table II).

Unfortunately, there is almost no way to check the two programs

externally. The only experimental parameters which can be used for

calibration are the ones observed by Closs for the cyclopentanediyl

(2).[10] As shown in Table II, these values are significantly lower

than the ones calculated using the programs. However the discrepancy

may simply be due to an inappropriate geometry.[20] For this reason, a

more extensive series of calculations needs to be performed on the system. It is worth noting that the related systems, 5 and 6, are predicted to have rather similar zero-field splitting parameters (Table II).

5

6

Table II. Zero-field splitting parameters calculated using the numerical integration method. The geometries and wavefunctions for the biradicals are explained in Refs. 20 and 21.

Biradical	Basis Orbital Size (Å/side)	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	Normalization Integral
2	[experimental value]	0.084	0.0020	------
	0.5	0.124	0.0072	0.846
5	0.5	0.122	0.0067	0.858
	0.4	0.122	0.0066	0.932
6	0.5	0.102	0.0020	0.871

References and Notes

1. For a review of the theoretical and experimental aspects of zero-field splitting parameters, see J.E. Wertz and J.R. Bolton, ''Electron Spin Resonance Elementary Theory and Practical Applications'', McGraw-Hill: New York, 1972.

2. M. Godfrey, C.W. Kern, and M. Karplus, J. Chem. Phys., 44, 4459 (1966).

3. J.H. van der Waals and G. ter Maten, Mol. Phys., 8, 301 (1964).

4. A.G. Motten, E.R. Davidson, and A.L. Kwiram, J. Chem. Phys., 75, 2603 (1981); D. Feller, W.T. Borden, and E.R. Davidson, J. Chem. Phys., 74, 2256 (1981), and references cited therein.

5. R. McWeeny, J. Chem. Phys., 34, 399 (1961).

6. J.A. Berson, R.J. Bushby, J.M. McBride, and M. Tremelling, J. Am. Chem. Soc., 93, 1544 (1971); M. Tremelling and J.M. McBride, unpublished work.

7. D.A. Dougherty and J.A. Berson, unpublished work.

8. L. Salem and C. Rowland, Angew. Chem. Int. Ed., Engl., 11, 92 (1972).

9. One notable exception is the work by Dougherty and Berson.[7]

10. S.L. Buchwalter and G.L. Closs, J. Am. Chem. Soc., 101, 4688 (1979).

11. See Section III.

12. See Section IV.

13. The program used for these calculations was an adaptation

of the one developed by Dougherty and Berson.[7]

14. Huckel Molecular orbitals appear to be adequate for the treatment of planar delocalized triplets.[7]

15. This discussion closely follows that of Dougherty.[7]

16. If there are N boxes along one dimension, the corresponding component of the box-to-box vector can vary from (1-N) to (N-1) — a total of (2N-1) possibilities. This figure must be raised to the power of three because of the three Cartesian axes.

17. In practice, the only significant saving is in the calculation of the weighting coefficients, since this operation must be performed N^6 times. In fact, it may be advantageous to generate redundant amplitudes because of savings which can later be realized in the evaluation of the weighting factors.

18. It can be shown that the off-diagonal elements of D do not have to be calculated for π-biradicals with C_{2v} symmetry. This is true only if the Cartesian axes are made to coincide with the symmetry axes. See the program in Appendix D.

19. As currently written the program in Appendix D does require the molecules to be oriented in a particular way. Only in this way can symmetry be used to its full advantage.

20. The geometry of 2 was optimized, within certain limits, by Schaefer: M.P. Conrad, R.M. Pitzer, and H.F. Schaefer, J. Am. Chem. Soc., 101, 2245 (1979). The orbitals for this system were obtained through a Restricted Hartree-Fock (RHF) calculation which was performed with a valence double-zeta basis set (see Section II).

21. The central angle in **5** was set at 102° to coincide with
    that in **2**. Similarly the five-membered ring in **6** was
    fixed at the Schaefer geometry for **2**.[20] The geometry
    of the cyclopropane ring was optimized by MNDO. Both the
    MNDO and RHF calculations on **6** were carried out by
    Lisa McElwee-White.

Appendix A

Description of Input Data for Zero-field Splitting Programs

1. __Title Card__

    TITLE

    FORMAT(A80)

2. __Control Parameter__

    PCCARD

    FORMAT(I2)

    PCCARD   number of primitive control cards

3. __Primitive Control Cards__

    DO I=1, PCCARD

    PCATOM(I), PCS(I), PCP(I)

    FORMAT (3I5)

    PCATOM(I)   number of atoms with primitive

                                control scheme I

    PCS(I)   number of s-type primitives centered

                                at each atom with primitive control

                                scheme I

    PCP(I)   number of p_x-type primitives centered

                                at each atom with primitive control

                                scheme I (it is assumed that the

                                number of P_x, P_y and P_z functions

are the same)

4. Specifications of Integration Grid

XMIN, XMAX, XSTEP

YMIN, YMAX, YSTEP

ZMIN, ZMAX, ZSTEP

FORMAT (3F10.3)

XMIN, YMIN, ZMIN	the minimum x,y, and z values in the integration grid (in Å)
XMAX, YMAX, ZMAX	the maximum x,y, and z values in the integration grid (in Å)
XSTEP, YSTEP, ZSTEP	the x,y, and z distances between points in the integration grid (in Å)

5. Atomic Coordinates

DO I=1, NATOM

ATX(I), ATY(I), ATX(I)

FORMAT (23X, 3D16.8)

NATOM	total number of atoms (calculated internally)
ATX(I)	x coordinate of the I-th atom (in Å)
ATY(I)	y coordinate of the I-th atom (in Å)
ATZ(I)	z coordinate of the I-th atom (in Å)

(Note: the format was chosen to conform with that on an

MQM: INTGEN.LIS output)

6. Primitive List

DO I=1, NPRIM

PFUNC(I), PEXP(I), PCOEF(I)

FORMAT (22X, I2, 2F15.7)

NPRIM	total number of primitive functions (calculated internally)
PFUNC(I)	basis function corresponding to the I-th primitive
PEXP(I)	exponent of the I-th primitive
PCOEF(I)	coefficient of the I-th primitive

(Note: the format was chosen to conform with that on an

MQM: INTGEN.LIS output)

7. Basis Function Coefficients

DO I=1, NBF

ABFCOF(I)

FORMAT(D15.8)

DO I=1, NBF

BBFCOF(I)

FORMAT (D15.8)

NBF	number of basis functions (calculated

internally)

ABFCOF(I)   coefficient of the I-th basis function

in orbital A

BBFCOF(I)   coefficient of the I-th basis function

in orbital B

(Note: A listing of coefficients with the proper format can

easily be obtained by using the MQMX: TRAN2P5 program)

Appendix B

Sample Input Deck

```
100    CALCULATION CF ZFS FOR TRIPETHYLENE // THETA = 102 DEG
200    2
300    2    10     5
400    6     4     C
500   -2.500       2.500      C.500 .
600   -2.000       3.000      C.500
700   -2.000       3.000      C.500
800    CP     C     C.COCOCCOOL+C0   1.1850C0C0C00+00   C.00C00000D+00
900    CL     C     C.CCCOCCOOD+C0  -1.1P5000C00D+00   0.000000000+00
1000   CM     C     C.CCCOCOCOL+C0   0.000000C00+00    9.595941C0D-01
1100   HPI    H     C.CCOOCCOOD+00   1.014486400+00   -1.076580300+00
1200   HRO    H     C.CCCOCOCOr+C0   2.202602700+00    3.906211000-01
1300   HLI    H     0.CC000C00D+C0  -1.014486400+00   -1.076580300+00
1400   HLO    H     C.CCCOC2C0D+C0  -2.202602700+00    3.906211000-C1
1500   HMU    H     8.P73859000-01   0.00000000D+00    1.592560300+00
1600   HMD    H    -8.P73859C00-C1   0.000000C00+C0    1.592560300+00
1700   CR    S     1    4233.0000C000      0.0012200
1800   CR    S     1     634.9000C00       C.0093420
1900   CR    S     1     146.1000C00       0.0454520
2000   CR    S     1      42.5000C00       0.1546570
2100   CR    S     1      14.1900C00       0.3588659
2200   CR    S     1       5.1480CCC       0.4386319
2300   CR    S     1       1.9670CCC       0.1459180
2400   CR    S     2       5.1480CCC      -C.1683670
2500   CR    S     2       0.4962000       1.0600907
2600   CR    S     3       0.1533CC0       1.C0C0000
2700   CR    X     4      18.1600C000      0.0185390
2800   CR    X     4       3.986CCC0       0.1154360
2900   CR    X     4       1.143CCC0       C.3861880
3000   CR    X     4       0.3594000       0.6401140
3100   CR    X     5       0.1146000       1.0000000
3200   CR    Y     6      18.1600C00       0.0185390
3300   CR    Y     6       3.986C0C0       0.1154360
3400   CR    Y     6       1.143CCC0       C.3861880
3500   CR    Y     6       0.3594000       C.6401140
3600   CR    Y     7       0.1146000       1.C0C0000
3700   CR    Z     8      18.1600C0C0      0.0185390
3800   CR    Z     8       3.986C0C0       0.1154360
3900   CR    Z     8       1.143CCC0       0.3861880
4000   CR    Z     8       0.3594000       C.64C1140
4100   CR    Z     9       0.1146000       1.0000000
4200   CL    S    10    4233.C00C000      0.C012200
4300   CL    S    10     634.9000C00       0.0093420
4400   CL    S    10     146.1000C00       C.0454520
4500   CL    S    10      42.5000C00       C.1546570
4600   CL    S    10      14.1900C0C       C.3588659
4700   CL    S    10       5.1480C0C       0.4386319
4800   CL    S    10       1.967CCC0       C.1459180
4900   CL    S    11       5.1480C000     -C.1683670
5000   CL    S    11       0.4962000       1.0600907
5100   CL    S    12       0.1533C00       1.0000000
5200   CL    X    13      18.1600CCC0      C.0185390
5300   CL    X    13       3.986CCC0       0.1154360
5400   CL    X    13       1.143CCC0       C.3861880
5500   CL    X    13       0.3594000       C.6401140
5600   CL    X    14       0.1146000       1.C0C0000
5700   CL    Y    15      18.1600CC0       0.0185390
5800   CL    Y    15       3.986CCC0       C.1154360
5900   CL    Y    15       1.143CCC0       0.3861880
6000   CL    Y    15       0.3594000       C.6401140
6100   CL    Y    16       0.1146000       1.C0C0000
6200   CL    Z    17      18.1600C0C0      0.0185390
6300   CL    Z    17       3.986CCC0       0.1154360
6400   CL    Z    17       1.143CCC0       0.3861880
6500   CL    Z    17       0.3594000       0.6401140
6600   CL    Z    18       0.1146C00       1.C0C0000
6700   CM    S    19    4233.C00C000      0.0012200
6800   CM    S    19     634.9000C00       C.0093420
6900   CM    S    19     146.1000C0C       C.0454520
7000   CM    S    19      42.5000C00       C.1546570
7100   CM    S    19      14.1900C00       C.3588659
7200   CM    S    19       5.1480C0C       0.4386319
7300   CM    S    19       1.967C0C0       0.1459180
7400   CM    S    20       5.1480C00      -0.1683670
7500   CM    S    20       0.4962000       1.0600907
7600   CM    S    21       0.1533C00       1.0000000
7700   CM    X    22      18.1600C00       C.0185390
7800   CM    X    22       3.986C0C0       0.1154360
7900   CM    X    22       1.143CCC0       C.2861880
8000   CM    X    22       0.3594CC0       C.64C1140
8100   CM    X    23       0.1146000       1.0000000
8200   CM    Y    24      18.1F0C0C0       0.0185390
8300   CM    Y    24       3.986C0C0       0.1154360
8400   CM    Y    24       1.143CCC0       C.3861880
8500   CM    Y    24       0.3594C00       0.6401140
```

```
8600   CN    Y    25    0.1146000    1.0000000
8700   CN    7    26   18.1600000    0.0185390
8800   CN    7    26    2.9860000    0.1154360
8900   CN    7    26    1.1430000    0.3861880
9000   CN    7    26    0.3590000    0.6401140
9100   CN    7    27    0.1146000    1.0000000
9200   HRI   S    28   19.2405600    0.0328280
9300   HRI   S    28    2.8991520    0.2312083
9400   HRI   S    29    0.6534101    0.8172381
9500   HRI   S    29    0.1775765    1.0000000
9600   HRO   S    30   19.2405600    0.0328280
9700   HRO   S    30    2.8991520    0.2312083
9800   HRO   S    30    0.6534101    0.8172381
9900   HRO   S    31    0.1775765    1.0000000
10000  HLI   S    32   19.2405600    0.0328280
10100  HLI   S    32    2.8991520    0.2312083
10200  HLI   S    32    0.6534101    0.8172381
10300  HLI   S    33    0.1775765    1.0000000
10400  HLO   S    34   19.2405600    0.0328280
10500  HLO   S    34    2.8991520    0.2312083
10600  HLO   S    34    0.6534101    0.8172381
10700  HLO   S    35    0.1775765    1.0000000
10800  HMU   S    36   19.2405600    0.0328280
10900  HMU   S    36    2.8991520    0.2312083
11000  HMU   S    36    0.6534101    0.8172381
11100  HMU   S    37    0.1775765    1.0000000
11200  HMD   S    38   19.2405600    0.0328280
11300  HMD   S    38    2.8991520    0.2312083
11400  HMD   S    38    0.6534101    0.8172381
11500  HMD   S    39    0.1775765    1.0000000
11600       0.0000000000D+00
11700       0.0000000000D+00
11800       0.0000000000D+00
11900       0.5361277800+00
12000       0.3110550200+00
12100       0.0000000000+00
12200       0.0000000000+00
12300       0.0000000000+00
12400       0.0000000000+00
12500       0.0000000000+00
12600       0.0000000000+00
12700       0.0000000000+00
12800       0.5361277800+00
12900       0.3110550200+00
13000       0.0000000000+00
13100       0.0000000000+00
13200       0.0000000000+00
13300       0.0000000000+00
13400       0.0000000000+00
13500       0.0000000000+00
13600       0.0000000000+00
13700       0.0000000000+00
13800       0.0000000000+00
13900       0.0000000000+00
14000       0.0000000000+00
14100       0.0000000000+00
14200       0.0000000000+00
14300       0.0000000000+00
14400       0.0000000000+00
14500       0.0000000000+00
14600       0.0000000000+00
14700       0.0000000000+00
14800       0.0000000000+00
14900       0.0000000000+00
15000       0.0000000000+00
15100       0.0000000000+00
15200       0.0000000000+00
15300       0.0000000000+00
15400       0.0000000000+00
15500       0.0000000000+00
15600       0.0000000000+00
15700       0.0000000000+00
15800       0.5044624900+00
15900       0.3023530000+00
16000       0.0000000000+00
16100       0.0000000000+00
16200       0.0000000000+00
16300       0.0000000000+00
16400       0.0000000000+00
16500       0.0000000000+00
16600       0.0000000000+00
16700       0.5044624900+00
16800       0.3023530000+00
16900       0.0000000000+00
17000       0.0000000000+00
```

```
17100    0.00000000D+00
17200    0.00000000D+00
17300    0.00000000D+00
17400    0.00000000D+00
17500    0.00000000D+00
17600    0.52442203D-01
17700    0.11055247D+00
17800    0.00000000D+00
17900    0.00000000D+00
18000    0.00000000D+00
18100    0.00000000D+00
18200    0.00000000D+00
18300    0.00000000D+00
18400    0.00000000D+00
18500    0.00000000D+00
18600    0.00000000D+00
18700    0.00000000D+00
18800    0.00000000D+00
18900    0.00000000D+00
19000    0.10445852D+00
19100    0.15379163D+00
19200    0.10445852D+00
19300    0.15379163D+00
```

Appendix C

ZFS2: A Program for Calculating Zero-field Splitting Parameters in Systems Without Symmetry

```
1CC    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
2CC    C                                                                   C
3CC    C        ZERC-FIELC SPLITTING PARAMETER PRCCRAM NUMRER TWO          C
4CC    C                                                                   C
5CC    C              ALTHCP : AARFN CCLDRERG                              C
6CO    C              DATF   : JUNE    1982                                C
7CC    C              PLRPCSE: CALCULATFS ZFS PY NUMFRICAL INTEGRATION     C
8CO    C                                                                   C
9C0    CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
1C00   C
1100   C
1200         IMPLICIT REAL*8 (A-H,O-Z)
130C         CHARACTER*EC TITLE
14C0         DIMENSION A(6),X(3,3),D(3),F(3),ATX(30),ATY(30),ATZ(30),PEXP(500),
15CC        1PCOFF(5CO),ARFCCF(50C),RRFCCF(500),ANORM(500),RNORM(500)
16CC         DIMENSION PAMP(5COCO),PAMP(5CCCC),PTCO(4C0000),NSPCA(30)
17CC         INTFGER*4 PCCARD,PCATOM(5),PCS(5),PCP(5),XDIM,YDIM,ZDIM,
18C0        1SEFIRST,SLAST,PXFIRST,PXLAST,PYFIRST,PYLAST,PZFIRST,PZLAST,
1850        1ITCTDIM,PFUNC(5CO)
19C0         PI=3.141592654
20C0         HALFPI=PI/2.0
2100         RCHR=0.5291771
2200         NHEAVY=0
23CC         NPPIM=C
240C         NATOM=0
2500         READ (22,810) TITLE
26C0         READ (22,815) PCCARD
2700   C
28CC   CCCCCC READ IN PRIMITIVE CONTROL CARDS
2SC0   C
3CC0         DO 100 I=1,PCCARD
3100         READ (22,8C1) PCATOM(I),PCS(I),PCP(I)
32C0         NATOM=NATOM+PCATOM(I)
33C0         NPPIM=NPPIM+PCATOM(I)*(PCS(I)+3*PCP(I))
340C   100   IF (PCP(I).NE.C) NHEAVY=NHEAVY+PCATOM(I)
3500         NNNN=0
36C0         DO 108 I=1,PCCARD
3700         DO 1C6 J=1,PCATOM(I)
3PCC         NNNN=NNNN+1
39C0         NSPCA(NNNN)=I
4CC0   1C6   CONTINUF
41C0   108   CONTINUE
42C0   C
43C0   CCCCCC READ IN DIMENSIONS OF INTEGRATION SPACE
44C0   C
45CC         READ (22,8C2) XMIN,XMAX,XSTEP
46CC         XMIN=XMIN/RCHR
47C0         XMAX=XMAX/RCHR
4PC0         XSTEP=XSTEP/ROHR
45C0         READ (22,8C2) YMIN,YMAX,YSTEP
5C0C         YMIN=YMIN/RCHR
5100         YMAX=YMAX/RCHR
5200         YSTEP=YSTEP/ROHR
5300         READ (22,8C2) ZMIN,ZMAX,ZSTEP
54C0         ZMIN=ZMIN/RCHR
55C0         ZMAX=ZMAX/RCHR
56C0         ZSTEP=ZSTEP/ROHR
5700         XDCD=(XMAX-XMIN)/XSTEP+1.0
5750         XDIM=NINT(XCDD)
5PC0         YCCD=(YMAX-YMIN)/YSTEP+1.0
5P5C         YDIM=NINT(YCDD)
59C0         ZDCD=(ZMAX-ZMIN)/ZSTEP+1.0
5S50         ZDIM=NINT(ZDDD)
6CC0   C
61CC   CCCCCC READ IN ATCMIC COORDINATES
62C0   C
6300         DO 110 I=1,NATCM
64CC         READ (22,PC3) ATX(I),ATY(I),ATZ(I)
65CC         ATX(I)=ATX(I)/RCHR
6FCC         ATY(I)=ATY(I)/RCHR
6700   110   ATZ(I)=ATZ(I)/RCHR
6P00   C
6SC0   CCCCCC READ IN PRIMITIVE LIST
7CC0   C
71CC         DO 12C I=1,NPPIM
72CC         READ (22,8C4) PFUNC(I),PEXP(I),PCOFF(I)
73CC   12C   NPF=PFUNC(I)
7400   C
75CC   CCCCCC READ IN BASIS FUNCTION COEFFICIENTS
76C0   C
77CC         DO 130 I=1,NPF
7PCC   13C   READ (22,8C5) ARFCCF(I)
7SCC         DO 135 I=1,NPF
PCC0   135   READ (22,8C5) RRFCCF(I)
8100         PZLAST=C
```

```
8400    C  *********************************************************************************
8500    C*****   *                                                                        *
8600    C       *            CALCULATION CF AMPLITUDE ARRAYS                              *
8700    C*****   *********************************************************************************
8800    C
8900            TOTDIM=XDIM*YDIM*ZDIM
9000            NTDIMP=TCTDIM+1
9100            NLSIZE=2*ZDIM-1
9200            NVSIZE=2*XDIM-1
9300            NWSIZE=2*YDIM-1
9400            NSSIZE=NWSIZE*NLSIZE
9500            NTWTCO=NVSIZE*NSSIZE
9600            DO 207 IJK=1,TCTDIM
9700            AAMP(IJK)=C.0
9800            PAMP(IJK)=C.0
9900    207     WTCO(IJK)=C.0
10000           DO 209 LMN=NTDIMP,NTWTCO
10100   209     WTCO(LMN)=C.0
10200           DC 399 IA=1,NATOM
10300           NPOINT=0
10400           IF (PCP(NSPCA(IA)).EC.C) GO TO 300
10500   C
10600   C*****   ***********************************************  << HEAVY ATOM SETUP >>   ******
10700   C
10800           SFIRST=PZLAST+1
10900           SLAST=PZLAST+PCS(NSPCA(IA))
11000           PXFIRST=SLAST+1
11100           PXLAST=SLAST+PCP(NSPCA(IA))
11200           PYFIRST=PXLAST+1
11300           PYLAST=PXLAST+PCP(NSPCA(IA))
11400           PZFIRST=PYLAST+1
11500           PZLAST=PYLAST+PCP(NSPCA(IA))
11600           DO 225 II=SFIRST,SLAST
11700           PNCRM=FCCEF(II)*(HALFPI/PEXP(II))**-0.75
11800           ANCRM(II)=APFCCF(PFUNC(II))*PNCRM
11900   225     BNORM(II)=BBFCCF(PFUNC(II))*PNCRM
12000           DO 226 JJ=PXFIRST,PXLAST
12100           PNCRM=PCCEF(JJ)*(((HALFPI/PEXP(JJ))**1.5)/(4.0*PEXP(JJ)))**-0.5
12200           ANCRM(JJ)=APFCCF(PFUNC(JJ))*PNCRM
12300   226     BNORM(JJ)=BBFCCF(PFUNC(JJ))*PNORM
12400           DO 227 KK=PYFIRST,PYLAST
12500           PNORM=PCCEF(KK)*(((HALFPI/PEXP(KK))**1.5)/(4.0*PEXP(KK)))**-0.5
12600           ANCRM(KK)=APFCCF(PFUNC(KK))*PNCRM
12700   227     BNORM(KK)=BBFCCF(PFUNC(KK))*PNCRM
12800           DO 228 LL=PZFIRST,PZLAST
12900           PNCRM=PCCEF(LL)*(((HALFPI/PEXP(LL))**1.5)/(4.0*PEXP(LL)))**-0.5
13000           ANORM(LL)=APFCCF(PFUNC(LL))*PNCRM
13100   228     BNCRM(LL)=BBFCCF(PFUNC(LL))*PNCRM
13200   C
13300   C*****   ***********************************************  << HEAVY ATOM VECTOR >>   *****
13400   C
13500   270     DO 298 I=1,XDIM
13600           XA=XMIN+XSTEP*(I-1)-ATX(IA)
13700           XA2=XA*XA
13800           DO 297 J=1,YDIM
13900           YA=YMIN+YSTEP*(J-1)-ATY(IA)
14000           XYA2=YA*YA+XA2
14100           DO 296 K=1,ZDIM
14200           ZA=ZMIN+ZSTEP*(K-1)-ATZ(IA)
14300           RA2=XYA2+ZA*ZA
14400           NPOINT=NPOINT+1
14500   C
14600   C*****   ***********************************************  << HEAVY ATOM CALC >>   ******
14700   C
14800           DO 230 IS=SFIRST,SLAST
14900           SSTOR=EXP(-1*PEXP(IS)*RA2)
15000           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IS)*SSTOR
15100   230     PAMP(NPOINT)=PAMP(NPOINT)+BNCRM(IS)*SSTOR
15200           DO 235 IPX=PXFIRST,PXLAST
15300           YSTOR=XA*EXP(-1*PEXP(IPX)*RA2)
15400           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IPX)*XSTOR
15500   235     PAMP(NPOINT)=PAMP(NPOINT)+PNCRM(IPX)*XSTOR
15600           DO 240 IPY=PYFIRST,PYLAST
15700           YSTOR=YA*EXP(-1*PEXP(IPY)*RA2)
15800           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IPY)*YSTOR
15900   240     PAMP(NPOINT)=PAMP(NPOINT)+PNCRM(IPY)*YSTOR
16000           DO 245 IPZ=PZFIRST,PZLAST
16100           ZSTOR=ZA*EXP(-1*PEXP(IPZ)*RA2)
16200           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IPZ)*ZSTOR
16300   245     PAMP(NPOINT)=PAMP(NPOINT)+PNCRM(IPZ)*ZSTOR
16400   296     CONTINUE
16500   297     CONTINUE
16600   298     CONTINUE
```

```
16700    C          CO TC 399
16800    C
16900    C*****    ************************************************  << LIGHT ATOM SETUP >>  ******
17000    C
17100      300    SFIRST=PZLAST+1
17200             SLAST=PZLAST+PCS(NSPCA(IA))
17300             PZLAST=SLAST
17400             DO 305 NN=SFIRST,SLAST
17500             PNORM=PCCEF(NN)*(HALFPI/PEXP(NN))**-0.75
17600             ANORM(NN)=APFCCF(PFUNC(NN))*PNORM
17700      305    BNORM(NN)=BHFCCF(PFUNC(NN))*PNORM
17800    C
17900    C*****    ************************************************  << LIGHT ATOM VECTOR >>  *****
18000    C
18100             DO 318 I=1,XDIM
18200             XA=XPIN+XSTEP*(I-1)-ATX(IA)
18300             XA2=XA*XA
18400             DO 317 J=1,YDIM
18500             YA=YPIN+YSTEP*(J-1)-ATY(IA)
18600             XYA2=YA*YA+XA2
18700             DO 316 K=1,ZDIM
18800             ZA=ZPIN+ZSTEP*(K-1)-ATZ(IA)
18900             RA2=XYA2+ZA*ZA
19000             NPCINT=NPOINT+1
19100    C
19200    C*****    ************************************************  << LIGHT ATOM CALC >>  ********
19300    C
19400             DO 310 IS=SFIRST,SLAST
19500             SSTOR=EXP(-I*PEXP(IS)*RA2)
19600             AAMP(NPCINT)=AAMP(NPCINT)+ANORM(IS)*XSTOR
19700      310    BAMP(NPOINT)=BAMP(NPCINT)+BNORM(IS)*XSTOR
19800      316    CONTINUE
19900      317    CONTINUE
20000      318    CONTINUE
20100      399    CONTINUE
20200      801    FORMAT (3I5)
20300      802    FORMAT (3F10.3)
20400      803    FORMAT (23X,3O16.8)
20500      804    FORMAT (22X,I2,2F15.7)
20600      805    FORMAT (D15.8)
20700      810    FORMAT (A8O)
20800      815    FORMAT (I2)
20900    C
21000    C*****    ************************************************************************************
21100    C*****    ************************************************************************************
21200    C*****    ************************************************************************************
21300    C
21400    C
21500    C*****    ***********************************************************************************+
21600    C          +                                                                              +
21700    C*****    +              EVALUATION OF WEIGHTING COEFFICIENTS                              +
21800    C          +                                                                              +
21900    C*****    ***********************************************************************************+
22000    C
22100             IPOINT=0
22200             ISPS2=YDIM*ZDIM
22300             INO=(XDIM-1)*NSSIZE+(YDIM-1)*NLSIZE+ZDIM
22400             DO 1600 IX=1,XDIM
22500             IN1=INO-IX*NSSIZE
22600             DO 1500 IY=1,YDIM
22700             IN2=IN1-IY*NLSIZE
22800             DO 1400 IZ=1,ZDIM
22900             IN3=IN2-IZ
23000             JPCINT=0
23100             IPOINT=IPOINT+1
23200             AAMPI=AAMP(IPOINT)
23300             BAMPI=BAMP(IPOINT)
23400             AXPI=AAMPI*BAMPI
23500             AAMPI2=AAMPI*AAMPI
23600             DO 1300 JX=1,XDIM
23700             IN4=IN3+JX*NSSIZE
23800             DO 1200 JY=1,YDIM
23900             IN5=IN4+JY*NLSIZE
24000             DO 1100 JZ=1,ZDIM
24100             JPCINT=JPCINT+1
24200             INDEX=IN5+JZ
24300             AAMPJ=AAMP(JPOINT)
24400             BAMPJ=BAMP(JPOINT)
24500             WTCO(INDEX)=WTCO(INDEX)+AAMPI2*BAMPJ*BAMPJ-AXPI*BAMPJ*AAMPJ
24600     1100    CONTINUE
24700     1200    CONTINUE
24800     1300    CONTINUE
24900     1400    CONTINUE
25000     1500    CONTINUE
25100     1600    CONTINUE
```

```
25300     C+++++  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
25400     C+++++  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
25500     C+++++  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
25600     C
25700     C
25800     C22222  222222222222222222222222222222222222222222222222222222222222222222
25900     C22222  2                                                                2
26000     C22222  2        CALCULATICN OF C-TENSCR ELEMENTS                         2
26100     C       2                                                                2
26200     C22222  222222222222222222222222222222222222222222222222222222222222222222
26300     C
26400     C
26500            SCALE=0.C
26550            XXINC=XSTEP*XSTEP
26575            YYINC=YSTEP*YSTEP
26587            ZZINC=ZSTEP*ZSTEP
26593            XYINC=XSTEP*YSTEP
26596            XZINC=XSTEP*ZSTEP
26598            YZINC=YSTEP*ZSTEP
26599            XYZINC=XSTEP*YSTEP*ZSTEP
26600            INDYC=(NSSIZE+NLSIZE)*-1
26700            DO 2000 I=1,6
26800     2000    A(I)=0.C
26900            DO 2500 I=1,NVSIZE
27000            ICX=I-XDIM
27100            IDXX=ICX*ICX
27200            ICX3=3*ICX
27250            FDXX=ICXX*XXINC
27300            FDXX3=FDXX*3.0
27400            INCY1=INCYC+I*NSSIZE
27500            DO 2400 J=1,NWSIZE
27600            IDY=J-YDIM
27650            IDY3=3*ICY
27700            IDYY=IDY*ICY
27800            FDXY3=ICX3*IDY*XYINC
27850            FDYY=IDYY*YYINC
27900            FDYY3=3.C*FDYY
28000            IDXXYY=ICXX+IDYY
28050            FDXXYY=FCXX+FDYY
28100            INDY2=INCY1+J*NLSIZE
28200            DO 2300 K=1,NLSIZE
28300            IDZ=K-ZDIM
28400            ICZZ=IDZ*ICZ
28500            IDPR=ICXXYY+IDZZ
28525            INDEX=INDY2+K
28537            GWTCC=WTCO(INDEX)
28543            SCALE=SCALE+GWTCO
28560            IF (IDRR.EC.0) GO TO 2300
28575            FDZZ=ICZZ*ZZINC
28600            DIST2=FDXXYY+FCZZ
28700            DIST5=DIST2**2.5
29000            A(1)=A(1)+GWTCC*(DIST2-FDXX3)/DIST5
29100            A(2)=A(2)-GWTCC*FDXY3/DIST5
29200            A(3)=A(3)+GWTCC*(DIST2-FDYY3)/DIST5
29300            A(4)=A(4)-GWTCC*IDX3*IDZ*XZINC/DIST5
29400            A(5)=A(5)-GWTCC*IDY3*ICZ*YZINC/DIST5
29500            A(6)=A(6)+GWTCC*(DIST2-3.0*FDZZ)/DIST5
29700     2300    CONTINUE
29800     2400    CONTINUE
29900     2500    CONTINUE
30000            DO 3000 I=1,6
30100            A(I)=A(I)*5.8571593/SCALE
30200     3000    CONTINUE
30250            APNORM=SCALE*XYZINC*XYZINC
30300            WRITE (27,4820)
30400            WRITE (27,5100)
30500            WRITE (27,5200)
30600            WRITE (27,4820)
30700            WRITE (27,810) TITLE
30800            WRITE (27,4820)
30900            WRITE (27,4820)
31000            WRITE (27,5300) XDIM,YDIM,ZDIM
31100            WRITE (27,4820)
31200            WRITE (27,4706)
31300            WRITE (27,4707)
31400            WRITE(27,4708)(A(I),I=1,6)
31500            WRITE(27,4820)
31600            N=3
31700     C
31800     C****** CALLING MATRIX DIAGONALIZATION SUBROUTINE
31900     C
32000            CALL SCIAG(N,A,X,D,E)
32100     C
32200     C****** FINAL OUTPUT
```

```
32300    C
32400            WRITE(27,4709)
32500            WRITE(27,4711)(D(I),I=1,3)
32600            WRITE(27,4820)
32700            WRITE(27,4712)
32800            DO 3110 I=1,3
32900            WRITE(27,4713)(X(I,J),J=1,3)
33000    3110    CONTINUE
33100            WRITE(27,4820)
33200            DO 3120 I=1,3
33300            C(I)=ABS(D(I))
33400    3120    CONTINUE
33500            IF (D(1).LE.D(3)) GO TO 3200
33600            CSAV=D(3)
33700            D(3)=D(1)
33800            D(1)=CSAV
33900    3200    EFIN=0.0
34000    3212    DFIN=D(3)*1.5
34100            EFIN=ABS(D(1)-D(2))*0.5
34200            WRITE(27,4714) DFIN
34300            WRITE(27,4715) EFIN
34350            WRITE(27,4820)
34375            WRITE(27,4877) SCALE
34387            WRITE(27,4878) ABNORM
34400    4701    FORMAT(20A4)
34500    4706    FORMAT(' D TENSOR ELEMENTS ARE :')
34600    4707    FORMAT('    XX       XY       YY       XZ       YZ       ZZ')
34700    4708    FORMAT(6F10.6)
34800    4709    FORMAT(' DIAGONALIZED D TENSOR ELEMENTS ARE :')
34900    4711    FORMAT(3F10.6)
35000    4712    FORMAT(' EIGENVECTORS OF D TENSOR :')
35100    4713    FORMAT(3F10.6)
35200    4714    FORMAT(' (D)/HC = ',F10.6)
35300    4821    FORMAT(' ',F10.6)
35400    4820    FORMAT(' ')
35500    4715    FORMAT(' (E)/HC = ',F10.6)
35600    4720    FORMAT(' ')
35700    5100    FORMAT('          CALCULATION OF ZERO-FIELD SPLITTING PARAMETERS')
35800    5200    FORMAT('          BY NUMERICAL INTEGRATION')
35900    5300    FORMAT(' GRID SIZE : ',I5,' X',I5,' X',I5)
35950    4877    FORMAT(' SCALING FACTOR : ',D15.8)
35975    4878    FORMAT(' NORMALIZATION : ',D15.8)
36000    9999    STOP
36100            END
36200    C
36300    C*******************************************************************
36400    C                                                                 *
36500    C           SDIAG : THE MATRIX DIAGONALIZATION SUBROUTINE         *
36600    C                                                                 *
37000    C*******************************************************************
37100    C
37200    C
37300    C
37400            SUBROUTINE SDIAG(N,A,X,D,E)
37500    C SDIAG DIAGONALIZES A REAL SYMMETRIC MATRIX
37600    C       METHOD - HOUSEHOLDER REDUCTION TO TRIDIAGONAL FORM, THEN QR
37700    C               ITERATIONS TO DIAGONALIZE
37800    C ARGONNE SUBROUTINE LIBRARY ROUTINE F255S
37900    C       MINOR MODIFICATIONS - LGV 1/76
38000    C
38100    C INPUT ARGUMENTS
38200    C N - DIMENSION OF MATRIX
38300    C A(N(N+1)/2) - MATRIX IN PACKED SYMMETRIC FORM   (IF N<0 THEN MATRIX
38400    C               IS ASSUMED TO BE ALREADY UNPACKED (N BY N))
38500    C X(N,N) - HOLDS ORDERED EIGENVECTORS ON OUTPUT (BY COLUMNS)
38600    C D(N) - HOLDS EIGENVALUES (SMALLEST FIRST) ON OUTPUT
38700    C E(N) - SCRATCH ARRAY
38800    C
38900            IMPLICIT REAL*8 (A-H,O-Z)
39000            REAL*8 EPS,A,D,X,E
39100            DIMENSION A(6),X(3,3),D(3),E(3)
39200            DATA EPS / 1.0-16/,ILIMIT /40/
39300            IF (N.LT.0) GO TO 96
39400            M = N*(N+1)/2 + 1
39500            DO 97 K = 1,N
39600            I = N-K+1
39700            DO 97 L = 1,I
39800            J = I-L+1
39900            M = M - 1
40000    97      X(I,J) = A(M)
40100            GO TO 100
40200    96      M = N
40300            N = -N
40400            DO 95 I = 1,N
40500            K = K + N
40600            DO 95 J = 1,I
```

```
40700     54    X(I,J) = A(K+J)
40800     C-----HOUSEHOLDER REDUCTION
40900     100   NM1 = N - 1
41000           DO 101 NN = 1,NM1
41100           I = N +1 - NN
41200           M = I - 2
41300           F = X(I,I -1)
41400           G = F
41500           S = C.DO
41600           IF (M.LT.1) GOTO 99
41700           DO 102 K = 1,M
41800     102   S = S + X(I,K)*X(I,K)
41900     99    D(I) = S
42000           IF (S.EQ.C.DO) GO TO 103
42100           M = M + 1
42200           S = S + F * F
42300           G = DSQRT (S)
42400           IF (F.GE.0.DO) G = -G
42500           RH = S - F * G
42600           X(I,I-1) = F - G
42700           F = 0.DO
42800           IF (M .LT. 1) GOTO 105
42900           DO 107 J = 1,M
43000           X(J,I) = X(I,J)/ RH
43100           S = C.DO
43200           DO 108 K = 1,J
43300     108   S = S + X(J,K) * X(I,K)
43400           JP1 = J + 1
43500           IF (M.LT.JP1) GOTO 98
43600           DO 109 K = JP1,M
43700     109   S = S + X(K,J) * X(I,K)
43800     98    E(J) = S/RH
43900     107   F = F + S * X(J,I)
44000     99    F = F / (RH + RH)
44100           DO 110 J = 1,M
44200     110   E(J)= E(J) - F * X(I,J)
44300           DO 111 J = 1,M
44400           DO 111 K = 1,J
44500     111   X(J,K) = X(J,K) - X(I,J) * E(K) -X(I,K) * E(J)
44600     C-----END S NOT EQUAL TO ZERO
44700     103   E(I-1) = G
44800     101   CONTINUE
44900     C-----END I LOOP
45000     C-----ACCUMULATION  OF TRANSFORMATION  MATRICES
45100           D(1) = 0.DO
45200           E(N)= 0.DO
45300           R = C.DO
45400           F = 0.DO
45500           DO 200 I = 1,N
45600           M = I - 1
45700           IF (D(I).EC.0.DO)GOTO 201
45800           DO 202 J = 1,M
45900           S = 0.DO
46000           DO 203 K = 1,M
46100     203   S = S + X(I,K) * X(K,J)
46200           DO 202 K = 1,M
46300     C-----THE FOLLOWING NONSENSE STATEMENT IS NEEDED TO COMBAT COMPILER BUG
46400           L=K+1-K
46500     202   X(K,J) = X(K,J) - S * X(K,L)
46600     C-----END J LOOP
46700     201   D(I) = X(I,I)
46800           X(I,I) = 1.0DO
46900           IF (M.LT. 1 ) GOTO 200
47000           DO 204 J = 1,M
47100           X(I,J) = C.DO
47200     204   X(J,I) = 0.DO
47300     200   CONTINUE
47400     C-----END I
47500     C-----DIAGONALIZATION  OF THE TRIDIAGONAL MATRIX
47600           DO 205 L = 1,N
47700           J = C
47800           RH = EPS * (DABS (D(L)) +  DABS (E(L)))
47900           IF (RH .LE. R) GOTO 206
48000           R = RH
48100     C-----TEST FOR SPLITTING
48200     206   DO 207 MM = L,N
48300           M = MM
48400           IF (DABS (F(M)) .LT. R) GOTO 208
48500     207   CONTINUE
48600     C-----LABEL 208 IS TEST FOR CONVERGENCE
48700     208   IF (M .EC. L) GOTO 209
48800     C-----LABEL 209 IS CONVERGENCE
48900     C-----LABEL 210 IS SHIFT
49000     210   P = .5DO *(D(L+1)- D(L))
49100           P = DSQRT (P * P + E(L)* E(L))
```

```
49200          RH = D(L) + P - P
49300          IF (P .LT. 0.D0) RH=RH+P+P
49400          DO 213 I = L,N
49500      213 D(I) = D(I) - RH
49600          F = F + RH
49700 C------OR TRANSFORMATION
49800          J = J + 1
49900          P = C(M)
50000          C = 1.D00
50100          S = 0.D0
50200          MML = M - L
50300          DO 214 II = 1,MML
50400          I = M - II
50500          R = DSQRT (P*P + E(I) * E(I))
50600          G = C * E(I)
50700          RH = C * P
50800          E(I+1) = S*R
50900          C = P/R
51000          S = E(I)/R
51100          D(I+1) = RH + S * (C * G + S * D(I))
51200          DO 214 K = 1,N
51300          RH = X(K,I+1)
51400          P = C * D(I) - S*G
51500          X(K,I+1) = X(K,I) * S + RH * C
51600      214 X(K,I) = X(K,I) * C - RH * S
51700 C------END K LOOP AND END I LOOP
51800      215 E(L) = S * P
51900          D(L) = C * P
52000          IF (DABS(E(L)) .LT. B) GOTO 209
52100          IF (J .LT. ILIMIT) GOTO 210
52200          GOTO 1000
52300 C------1000 IS ERROR RETURN INDICATING FAILURE OF QR TO CONVERGE
52400      209 D(L) = D(L)+ F
52500      205 CONTINUE
52600 C------END L LOOP
52700 C------ORDERING OF EIGENVALUES
52800          DO 300 I = 1,N
52900          K = I
53000          P = D(I)
53100          IP1 = I + 1
53200          IF (N .LT. IP1) GOTO 301
53300          DO 302 J = IP1 , N
53400          IF (D(J) .GE. P) GOTO 302
53500          K = J
53600          P = D(J)
53700      302 CONTINUE
53800 C------END J LOOP
53900      301 IF (K.EQ.I) GOTO 300
54000          D(K) = D(I)
54100          D(I) = P
54200          DO 304 J = 1,N
54300          P = X(J,I)
54400          X(J,I) = X(J,K)
54500      304 X(J,K) = P
54600      300 CONTINUE
54700 C------END J,END K NOT EQUAL I, I, SDIAG
54800          RETURN
54900     1000 WRITE (6,1002)
55000     1002 FORMAT (//' *****  UNABLE TC DIAGONALIZE MATRIX  ***** ')
55100          STOP 8
55200          END
```

Appendix D

ZFS3: A Program for Calculating Zero-field Splitting Parameters in Systems With C_{2v} Symmetry

```
1CC      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
2CC      C                                                                C
3CC      C            ZERO-FIELD SPLITTING PARAMETER PROGRAM NUMBER THREE  C
4CC      C                                                                C
5CC      C            AUTHOR  : AARON GOLDBERG                            C
6CC      C            DATE    : JUNE    1982                              C
7CC      C            FUNCTION: CALCULATES ZFS BY NUMERICAL INTEGRATION    C
PCC      C                      FOR MOLECULES WITH C2V SYMMETRY.  THE      C
P5C      C                      Z-AXIS MUST BE THE UNIQUE AXIS.            C
950      C                   WRITES OUT SCALING FACTOR                     C
1CC0     C                                                                C
11CC     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
12C0     C
13C0     C
14C0            IMPLICIT REAL*8 (A-H,O-Z)
15C0            CHARACTER*8C TITLE
16C0            DIMENSION A(3),X(3,3),C(3),F(3),ATX(30),ATY(30),ATZ(30),PEXP(500),
17C0           1PCOEF(5CC),ABFCCF(500),ABFCOF(500),ANORM(500),BNORM(500)
18C0            DIMENSION AAMP(1C0C00),BAMP(1C0000),WTC0(1C0000),NSPCA(30)
19C0            INTEGER*4 PCCARD,PCATOM(5),PCS(5),PCP(5),XDIM,YDIM,ZDIM,
2CC0           1SFIRST,SLAST,PXFIRST,PXLAST,PYFIRST,PYLAST,PZFIRST,PZLAST,
21C0           1TOTDIM,PFUNC(500),XZERO,YZERO,ZZERO,XSTOP,YSTOP,ZSTOP,
22C0           1XSTOP1,YSTOP1
23C0            LOGICAL*4 CHECK1,CHECK2,CZECH1,CZECH2
24C0            PI=3.141592654
2=CC           HALFPI=PI/2.0
26C0            BOHR=0.5291771
27C0            NHEAVY=0
2PC0            NPRIM=0
29C0            NATOM=0
3CC0            READ (22,810) TITLE
31C0            READ (22,815) PCCARD
32C0     C
33C0     CCCCCC READ IN PRIMITIVE CONTROL CARDS
34C0     C
3=0C           DO 100 I=1,PCCARD
36C0            READ (22,8C1) PCATOM(I),PCS(I),PCP(I)
37C0            NATOM=NATOM+PCATOM(I)
3PC0            NPRIM=NPRIM+PCATOM(I)*(PCS(I)+3*PCP(I))
39C0     100    IF (PCP(I).NE.C) NHEAVY=NHEAVY+PCATOM(I)
4CC0            NNNN=0
41C0            DO 108 I=1,PCCARD
42C0            DO 106 J=1,PCATOM(I)
43C0            NNNN=NNNN+1
44C0            NSPCA(NNNN)=I
45CC     106    CONTINUE
46CC     108    CONTINUE
47C0     C
4PC0     CCCCCC READ IN DIMENSIONS OF INTEGRATION SPACE
49C0     C
5CC0            READ (22,8C2) XMIN,XMAX,XSTEP
51C0            XMIN=XMIN/BOHR
52C0            XMAX=XMAX/BOHR
53C0            XSTEP=XSTEP/BOHR
54C0            READ (22,8C2) YMIN,YMAX,YSTEP
55C0            YMIN=YMIN/BOHR
5FC0            YMAX=YMAX/BOHR
57C0            YSTEP=YSTEP/BOHR
5PC0            READ (22,8C2) ZMIN,ZMAX,ZSTEP
59C0            ZMIN=ZMIN/BOHR
6CC0            ZMAX=ZMAX/BOHR
61C0            ZSTEP=ZSTEP/BOHR
62C0            XDDD=(XMAX-XMIN)/XSTEP+1.0
63C0            XDIM=NINT(XDDD)
64C0            YDDD=(YMAX-YMIN)/YSTEP+1.0
6=CC           YDIM=NINT(YDDD)
66C0            ZDDD=(ZMAX-ZMIN)/ZSTEP+1.0
67C0            ZDIM=NINT(ZDDD)
6PC0            XSTOP=(XDIM+1)/2
6SC0            YSTOP=(YDIM+1)/2
7CC0            ZSTOP=ZDIM
71C0            XSTOP1=XSTOP+1
72C0            YSTOP1=YSTOP+1
73C0     C
74C0     CCCCCC READ IN ATOMIC COORDINATES
7=C0     C
76C0            DO 110 I=1,NATOM
77C0            READ (22,8C3) ATX(I),ATY(I),ATZ(I)
7PC0            ATX(I)=ATX(I)/BOHR
7SCC           ATY(I)=ATY(I)/BOHR
RCC0     110    ATZ(I)=ATZ(I)/BOHR
81C0     C
R2C0     CCCCCC READ IN PRIMITIVE LIST
R3C0     C
R4C0            DO 120 I=1,NPRIM
```

```
F6CC            READ (22,FC4) PFUNC(I),PEXP(I),PCCEF(I)
P6CC      120   NPF=PFLNC(I)
8700      C
RPCO      CCCCCC  READ IN BASIS FUNCTICN COEFFICIENTS
8SCC      C
9CCC            DO 130 I=1,NPF
9100      130   READ (22,PC5) ABFCCF(I)
9200            DO 135 I=1,NPF
93CC      135   READ (22,8C5) PPFCOF(I)
94CC            PZLAST=0
95CC      C
9600      C*****  **************************************************************
9700      C       *                                                           *
9800      C*****  *           CALCULATION CF AMPLITUDE ARRAYS                 *
9900      C       *                                                           *
1CCCC     C*****  **************************************************************
10100     C
102CC           TOTDIM=XCIM*YDIM*ZCIM
103CC           NTDIMP=TCTDIM+1
104CC           NLSIZE=2*ZCIM-1
10500           NVSIZE=2*XCIM-1
106CC           NWSIZE=2*YCIM-1
107CC           NSSIZE=NWSIZE*NLSIZE
108CC           NTWTCO=NVSIZE*NSSIZE
10900           DO 207 IJK=1,TCTDIM
11CCC           AAMP(IJK)=C.0
11100           BAMP(IJK)=C.0
112CC     207   WTCO(IJK)=C.0
113CC           DO 399 IA=1,NATOM
11400           NPOINT=0
11FCC           IF (PCP(NSPCA(IA)).EQ.0) GO TO 300
116CC     C
117CC     C*****  ******************************** << HEAVY ATOM SETUP >>  ******
118CC     C
11900           SFIRST=PZLAST+1
12CCC           SLAST=PZLAST+PCS(NSPCA(IA))
121CC           PXFIRST=SLAST+1
122CC           PXLAST=SLAST+PCP(NSPCA(IA))
123CC           PYFIRST=PXLAST+1
124CC           PYLAST=PXLAST+PCP(NSPCA(IA))
125CC           PZFIRST=PYLAST+1
126CC           PZLAST=PYLAST+PCP(NSPCA(IA))
127CC           DO 225 II=SFIRST,SLAST
128CC           PNCRM=PCCEF(II)*(HALFPI/PEXP(II))**-0.75
129CC           ANCRM(II)=ABFCCF(PFUNC(II))*PNCRM
13CCC     225   BNCRM(II)=BBFCCF(PFUNC(II))*PNCRM
13100           DO 226 JJ=PXFIRST,PXLAST
132CC           PNCRM=PCCEF(JJ)*(((HALFPI/PEXP(JJ))**1.5)/(4.0*PEXP(JJ)))**-0.5
133CC           ANCRM(JJ)=APFCCF(PFUNC(JJ))*PNCRM
134CC     226   BNCRM(JJ)=BBFCCF(PFUNC(JJ))*PNCRM
13500           DO 227 KK=PYFIRST,PYLAST
136CC           PNCRM=PCCEF(KK)*(((HALFPI/PEXP(KK))**1.5)/(4.0*PEXP(KK)))**-0.5
13700           ANCRM(KK)=APFCCF(PFUNC(KK))*PNCRM
138CC     227   BNCRM(KK)=BBFCCF(PFUNC(KK))*PNCRM
13900           DO 228 LL=PZFIRST,PZLAST
14CCC           PNCRM=PCCEF(LL)*(((HALFPI/PEXP(LL))**1.5)/(4.0*PEXP(LL)))**-0.5
14100           ANCRM(LL)=ABFCCF(PFUNC(LL))*PNCRM
142CC     228   BNCRM(LL)=BBFCCF(PFUNC(LL))*PNCRM
14300     C
144CC     C*****  ****************************************** << HEAVY ATOM VECTOR >>  *****
14500     C
146CC     22C   DO 258 I=1,XDIM
147CC           XA=XMIN+XSTEP*(I-1)-ATX(IA)
148CC           XA2=XA*XA
149CC           DO 297 J=1,YDIM
15CCC           YA=YMIN+YSTEP*(J-1)-ATY(IA)
15100           XYA2=YA*YA+XA2
15200           DO 296 K=1,ZDIM
15300           ZA=ZMIN+ZSTEP*(K-1)-ATZ(IA)
15400           RA2=XYA2+ZA*ZA
15500           NPOINT=NPOINT+1
15600     C
157CC     C*****  ****************************************** << HEAVY ATOM CALC >>  *******
158CC     C
159CC           DO 230 IS=SFIRST,SLAST
16CCC           SSTOR=EXP(-1*PEXP(IS)*RA2)
16100           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IS)*SSTOR
162CC     230   BAMP(NPOINT)=BAMP(NPOINT)+BNCRM(IS)*SSTOR
16300           DO 235 IPX=PXFIRST,PXLAST
164CC           XSTOR=XA*EXP(-1*PEXP(IPX)*RA2)
16500           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IPX)*XSTOR
166CC     235   BAMP(NPOINT)=BAMP(NPOINT)+BNCRM(IPX)*XSTOR
167CC           DO 24C IPY=PYFIRST,PYLAST
168CC           YSTOR=YA*EXP(-1*PEXP(IPY)*RA2)
169CC           AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IPY)*YSTOR
```

```
17000      240    PAMP(NPCINT)=PAMP(NPCINT)+PNCRM(IPY)*YSTOP
17100             CC 245 IP7=P7FIRST,P7LAST
17200             7STOP=ZA+FYP(-1*PFXP(IP7)*RA2)
17300             AAMP(NFCINT)=AAMP(NPCINT)+ANCRM(IP7)*7STOR
17400      245    BAMP(NPOINT)=BAMP(NPCINT)+PNCRM(IP7)*7STOP
17500      296    CONTINUE
17600      297    CONTINUE
17700      298    CONTINUE
17800             GC TC 399
17900   C
18000   C*****   ****************************************   << LIGHT ATOM SETUP >>   ******
18100   C
18200      300    SFIRST=PZLAST+1
18300             SLAST=PZLAST+PCS(NSPCA(IA))
18400             PZLAST=SLAST
18500             DC 305 NN=SFIRST,SLAST
18600             PNCRM=PCCEF(NN)*(HALFPI/PEXP(NN))**-0.75
18700             ANCRM(NN)=ARFCCF(PFUNC(NN))*PNORM
18800      305    BNCRM(NN)=PBFCCF(PFUNC(NN))*PNCRM
18900   C
19000   C*****   ****************************************   << LIGHT ATOM VECTOR >>   *****
19100   C
19200             DO 318 I=1,XDIM
19300             XA=XMIN+XSTEP*(I-1)-ATX(IA)
19400             XA2=XA*XA
19500             DO 317 J=1,YDIM
19600             YA=YMIN+YSTEP*(J-1)-ATY(IA)
19700             XYA2=YA*YA+XA2
19800             DO 316 K=1,ZDIM
19900             7A=ZMIN+ZSTEP*(K-1)-ATZ(IA)
20000             RA2=XYA2+7A*ZA
20100             NPOINT=NPOINT+1
20200   C
20300   C*****   ****************************************   << LIGHT ATOM CALC >>   ********
20400   C
20500             DO 310 IS=SFIRST,SLAST
20600             SSTOP=FXF(-1*PEXP(IS)*RA2)
20700             AAMP(NPOINT)=AAMP(NPOINT)+ANCRM(IS)*XSTOR
20800      310    BAMP(NPOINT)=BAMP(NPCINT)+BNCRM(IS)*XSTOR
20900      316    CONTINUE
21000      317    CONTINUE
21100      318    CONTINUE
21200      399    CONTINUE
21300      801    FCRMAT (3I5)
21400      802    FCRMAT (3F10.3)
21500      803    FORMAT (23X,3D16.8)
21600      804    FORMAT (22X,I2,2F15.7)
21700      805    FORMAT (D15.8)
21800      810    FORMAT (ARC)
21900      815    FORMAT (I2)
22000   C
22100   C*****   ********************************************************************************
22200   C*****   ********************************************************************************
22300   C*****   ********************************************************************************
22400   C
22500   C
22600   C+++++   ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
22700   C+++++   +                                                                              +
22800   C+++++   +              EVALUATION OF WEIGHTING COEFFICIENTS                            +
22900   C+++++   +                                                                              +
23000   C+++++   ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
23100   C
23200             ISHSZ=YDIM*ZDIM
23250   C
23275   C+++++   ++++++++++++++++++   << INCREMENT ELECTRON I OVER QUADRANT 1 >>   ++++++++++++
23287   C
23300             DO 1600 IX=1,XSTCP
23400             ISTRX=XSTCP-IX
23500             CZFCF1=ISTRX.FC.C
23600             INDY1=(IX-1)*ISHSZ
23700             DC 150C IY=1,YSTCP
23800             ISTRY=YSTCP-IY
23900             CZFCF2=ISTRY.FC.0
24000             INDY2=INCY1+(IY-1)*ZDIM
24100             CC 1400 I7=1,ZSTCP
24200             JPCINT=0
24300             TPCINT=INDY2+I7
24400             AAMPI=AAMP(IPCINT)
24500             BAMPI=BAMP(TPOINT)
24600             AXBI=AAMPI*BAMPI
24700             AAMPI2=AAMPI*AAMPI
24800             BAMPI2=BAMPI*BAMPI
24850   C
24875   C+++++   ++++++++++++++++++   << INCREMENT ELECTRON J OVER QUADRANT 1 >>   ++++++++++++
24887   C
```

```
24000          DO 1200 JX=1,XSTOP
25000          FACTR1=1.0
25100          JSTRX=JX-XSTOP
25200          IF (CZECH1.AND.(JSTRX.EQ.0)) FACTR1=C.5
25400          IN1=ABS(JX-IX)*ISHSZ+1
25500          DO 1170 JY=1,YSTOP
25600          FACTR2=1.0
25700          JSTRY=JY-YSTOP
25800          IF (CZECH2.AND.(JSTRY.EQ.0)) FACTR2=C.5
26000          FAX=FACTR1*FACTR2
26100          IN2=IN1+ABS(JY-IY)*ZDIM
26200          DO 1160 JZ=1,ZDIM
26600          INDEX=IN2+ABS(JZ-IZ)
26700          JPOINT=JPOINT+1
26800          AAMPJ=AAMP(JPOINT)
26900          BAMPJ=BAMP(JPOINT)
27000          WTCO(INDEX)=WTCO(INDEX)+(AAMPI2*BAMPJ*BAMPJ-AXBI*BAMPJ*AAMPJ)*FAX
27100   1160   CONTINUE
27200   1170   CONTINUE
27250 C
27275 C++++++  +++++++++++++++++++  << INCREMENT ELECTRON J OVER QUADRANT 2>> +++++++
27287 C
27300          DO 1190 JY=YSTOP1,YDIM
27400          FACTR2=1.0
27500          JSTRY=JY-YSTOP
27600          IF (CZECH2.AND.(JSTRY.EQ.0)) FACTR2=C.5
27800          FAX=FACTR1*FACTR2
27900          IN2=IN1+ABS(JY-IY)*ZDIM
28000          DO 1180 JZ=1,ZDIM
28400          INDEX=IN2+ABS(JZ-IZ)
28500          JPOINT=JPOINT+1
28600          AAMPJ=AAMP(JPOINT)
28700          BAMPJ=BAMP(JPOINT)
28800          QQQ=AAMPI2*BAMPJ*BAMPJ
28900          WTCO(INDEX)=WTCO(INDEX)+(QQQ-AXBI*BAMPJ*AAMPJ)*FAX
29000   1180   CONTINUE
29100   1190   CONTINUE
29200   1200   CONTINUE
29250 C
29275 C++++++  ++++++++++++  << INCREMENT ELECTRON J OVER QUADRANTS 3 AND 4 >>  ++++++++
29287 C
29300          DO 1300 JX=XSTOP1,XDIM
29400          FACTR1=1.0
29500          JSTRX=JX-XSTOP
29600          IF (CZECH1.AND.(JSTRX.EQ.0)) FACTR1=0.5
29800          IN1=ABS(JX-IX)*ISHSZ+1
29900          DO 1290 JY=1,YDIM
30000          FACTR2=1.C
30100          JSTRY=JY-YSTOP
30200          IF (CZECH2.AND.(JSTRY.EQ.0)) FACTR2=C.5
30400          FAX=FACTR1*FACTR2
30500          IN2=IN1+ABS(JY-IY)*ZDIM
30600          DO 1280 JZ=1,ZDIM
31000          INDEX=IN2+ABS(JZ-IZ)
31100          JPOINT=JPOINT+1
31200          AAMPJ=AAMP(JPOINT)
31300          BAMPJ=BAMP(JPOINT)
31400          QQQ=AAMPI2*BAMPJ*BAMPJ
31500          WTCO(INDEX)=WTCO(INDEX)+(QQQ-AXBI*BAMPJ*AAMPJ)*FAX
31600   1280   CONTINUE
31700   1290   CONTINUE
31800   1300   CONTINUE
31900   1400   CONTINUE
32000   1500   CONTINUE
32100   1600   CONTINUE
32200 C
32300 C++++++  +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
32400 C++++++  +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
32500 C++++++  +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
32600 C
32700 C
32800 Caaaaa  aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa
32900 C                                                                           a
33000 Caaaaa  a            CALCULATION OF D-TENSOR ELEMENTS                       a
33100 C                                                                           a
33200 Caaaaa  aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa
33300 C
33400 C
33500          SCALE=0.C
33600          INDEX=C
33650          XXINC=XSTEP*XSTEP
33700          YYINC=YSTEP*YSTEP
33687          ZZINC=ZSTEP*ZSTEP
33693          XYZINC=XSTEP*YSTEP*ZSTEP
337C0          DO 2000 I=1,3
```

```
33500    2000    A(I)=C.C
33900            DO 2500 I=1,XDIM
34C00            IDY=I-1
34100            IDXX=IDX*IDX
34150            FDXX=IDXX*XXINC
34200            FDXX3=FDXX*3.0
343C0            DO 2400 J=1,YDIM
34400            IDY=J-1
34500            IDYY=IDY*IDY
34550            FDYY=IDYY*YYINC
346C0            FDYY3=FDYY*3.0
347C0            IDXXYY=IDXX+IDYY
34750            FDXXYY=FDXX+FDYY
34800            DO 2300 K=1,ZDIM
349C0            INDEX=INDEX+1
35C00            IDZ=K-1
35100            IDZZ=IDZ*IDZ
35200            IDRR=IDXXYY+IDZZ
35250            GWTCC=WTCC(INDEX)
35275            SCALE=SCALE+GWTCO
355C0            IF (IDRR.EC.0) GO TO 2300
35350            FDZZ=IDZZ*ZZINC
354C0            DIST2=FDXXYY+FDZZ
35500            DIST5=DIST2**2.5
35700            A(1)=A(1)+GWTCO*(DIST2-FDXX3)/DIST5
358C0            A(2)=A(2)+GWTCC*(DIST2-FDYY3)/DIST5
35900            A(3)=A(3)+GWTCO*(DIST2-3.0*FDZZ)/DIST5
36100    2300    CONTINUE
362C0    2400    CONTINUE
36300    2500    CONTINUE
364C0            DO 3C00 I=1,3
36500            A(I)=A(I)*5.8571593/SCALE
366C0            A(I)=ABS(A(I))
36700    3000    CONTINUE
36750            ABNORM=SCALE*XYZINC*XYZINC*4.0
36800    C
369C0    C****** ORDERING OF D-TENSOR ELEMENTS
37000    C
37100            D(3)=MAX(A(1),A(2),A(3))
372C0            D(1)=MIN(A(1),A(2),A(3))
37300            IF (A(1).EC.D(3)) GO TO 3840
37400            IF (A(1).EC.D(1)) GO TO 3820
37500            D(2)=A(1)
37600            GO TO 3890
37700    3820    IF (A(2).EC.D(3)) GO TO 3830
37800            D(2)=A(2)
37900            GO TO 3850
38C00    3830    D(2)=A(3)
38100            GO TO 3890
38200    3840    IF (A(2).EC.D(1)) GO TO 3850
38300            D(2)=A(2)
38400            GO TO 3890
38500    3850    D(2)=A(3)
38600    C
38700    C****** FINAL OUTPUT
38800    C
38900    3890    WRITE (27,4820)
39C00            WRITE (27,5100)
39100            WRITE (27,5200)
39200            WRITE (27,4820)
39300            WRITE (27,P10) TITLE
39400            WRITE (27,4820)
39500            WRITE (27,4820)
396C0            WRITE (27,5300) XDIM,YDIM,ZDIM
39700            WRITE (27,4820)
398C0            WRITE(27,47C9)
39900            WRITE(27,4711)(D(I),I=1,3)
40C00            WRITE(27,4820)
40100    3200    EFIN=0.0
40200    3212    DFIN=D(3)*1.5
403C0            EFIN=ABS(D(1)-D(2))*C.5
40400            WRITE(27,4714) DFIN
40500            WRITE(27,4715) EFIN
40550            WRITE(27,4820)
40575            WRITE(27,4877) SCALE
40587            WRITE(27,4878) ABNORM
40600    4701    FORMAT(2CA4)
40700    4708    FORMAT(6F1C.6)
40800    47C9    FORMAT(' DIAGONALIZED D TENSOR ELEMENTS ARE :')
40900    4711    FORMAT(3F1C.6)
41C00    4712    FORMAT(3F1C.6)
41100    4714    FORMAT(' (D)/HC = ',F1C.6)
41200    4821    FORMAT(' ',F10.6)
41300    482C    FORMAT(' ')
41400    4715    FORMAT(' (E)/HC = ',F1C.6)
```

```
41500    4720    FORMAT(' ')
41600    510C    FORMAT('                    CALCULATION CF ZERO-FIELD SPLITTING PARAMETERS')
417C0    52CC    FORMAT('                       BY NUMERICAL INTEGRATION')
418C0    5300    FORMAT(' GRID SIZE : ',I5,'  X',I5,'  X',I5)
41850    4877    FORMAT(' SCALING FACTOR : ',D15.8)
41875    4878    FORMAT(' NORMALIZATION : ',D15.8)
41900    9999    STOP
42000            END
```