The Quintet State of a Partially Localized, Hydrocarbon Tetraradical: Cyclobutane as a General Ferromagnetic Coupling Unit

Thesis by

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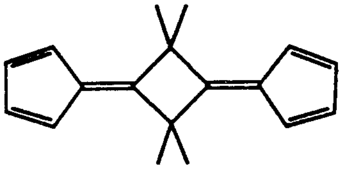
TABLE OF CONTENTS

The Quintet State of a Partially Localized, Hydrocarbon Tetraradical: Cyclobutane as a General Ferromagnetic Coupling Unit

Abstract

The partially localized tetraradical **22** has been generated at temperatures of 77 K and below in 2-methyltetrahydrofuran and poly(methylmethacrylate) matrices, and directly observed by EPR spectroscopy. The evolution of the EPR spectrum resulting from prolonged photolysis of the bisdiazene precursor **20** indicates a two-photon process, wherein a triplet spectrum (assigned unambiguously to the monoazobiradical) gradually gives way to a quintet spectrum, ascribed to the target tetraradical. The observed quintet state is tentatively identified as the ground state of the tetraradical, based on design considerations, the fact that the quintet spectrum is intense at temperatures as low as 3.8 K, and preliminary Curie Law studies. The thermal stability of **22** (indefinitely stable in the dark at 77 K) is an unexpected attribute of this molecule; no other cyclobutanediyl studied thus far has exhibited similar sturdiness at temperatures above *ca.* 60 K. Two synthetic routes to the prerequisite bisfulvene **15** are discussed.



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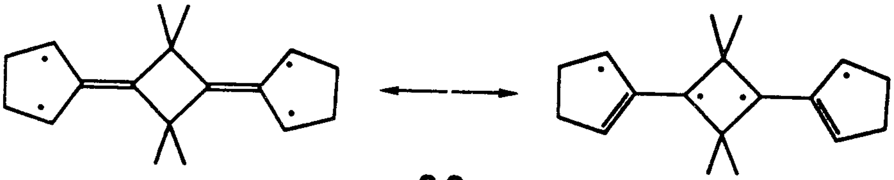

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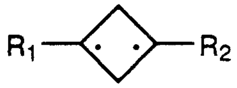
INTRODUCTION

While discrete molecules with quintet multiplicity and higher are known for fully delocalized species containing heteroatoms and/or carbene centers,[1] they are virtually unknown for hydrocarbon systems consisting of high spin units which are effectively isolated from one another. To a first approximation, there is no reason why non-conjugated free electrons should be correlated. However, non-conjugated does not necessarily imply non-interacting. Naturally, within a given separation, the spins will interact in a through-space, π fashion. Aside from this, however, free electrons which are not connected through classical π conjugation can (and do) interact substantially through admixture of their own orbitals with those of like symmetry in intervening, hyperconjugating groups. Such through-bond coupling accounts for some unexpected reversals in the ordering of state energies in saturated biradicals.[2] The current research was concerned with the enlistment of hyperconjugating groups to couple isolated, localized[3] high-spin units within a molecule, with a view to creating systems of unusually high multiplicities.

In recent years, the number of ground state triplet biradicals reported in the literature has grown impressively, largely due to the development of matrix isolation techniques, which make possible the direct observation of these highly reactive species.[4] The stringing of *successive* high-spin units together, however, with all spins parallel, has proven far more challenging. Limited success has been realized only in the areas of polycarbenes,[1a,c,d] polynitroxyls,[1b] and certain charge transfer salts.[5] Obviously, if a linker could be found which would couple high-spin units within a molecule, so that their spins were aligned in a parallel, rather than antiparallel fashion, systems of very high multiplicity could, in principle, be constructed from such alternating units. The discovery of such a ferromagnetically coupling linker could well lead to the logical extension of this model: the synthesis of a fully hydrocarbon ferromagnet.[6]

Assuming for now the availabilty of reasonably stable intrinsic triplets, the choice of linker then becomes important. If the linker enters into classical π conjugation with the high-spin units, at least two consequences may ensue: First, the linker may alter the total electronic energy of the system to the point where a closed shell form becomes the preferred ground state. Second, it is conceivable that extended conjugation and delocalization could lead to weaker exchange repulsions, and so diminish the triplet advantage. In view of the above considerations, it would appear that an "insulating" type linker *might* be a better candidate, i.e., one which effectively insulates one high-spin unit from another. The paradox, of course, is that one wants a linker which will both insulate the units, and couple them at the same time.

Unlikely as it may at first seem, research in our laboratories provided compelling evidence that such a specialized and powerful tool may actually exist. In anticipation of experimental confirmation, *ab initio* calculations performed in our research group concluded that the localized biradical, 1,3-cyclobutanediyl, **1a**, should have a triplet ground state,[7] for reasons which will be elaborated below. It was a disappointment, therefore, when photolysis of the appropriate diazene precursor to **1a** (in an organic matrix at cryogenic temperatures) failed to yield the triplet spectrum of the 1,3-diyl.[8] Subsequently, the diazene precursors to derivatives **1b-h** were synthesized and photolyzed in the cavity of an EPR spectrometer at cryogenic temperatures; all yielded triplet 1,3-cyclobutanediyls, as evidenced by their characteristic EPR spectra.[4g] Although the necessary experiments have not yet been performed which will establish that these are indeed ground state, and not thermally populated excited state triplets, the fact that signals are recorded at 4 K strongly suggests that one is observing the ground state. Thus, the original *ab initio* study has been vindicated.



1

a: $R_1 = R_2 = H$
b: $R_1 = R_2 = Me$
c: $R_1 = R_2 = Et$
d: $R_1 = R_2 = n\text{-}Pr$
e: $R_1 = R_2 = Ph$
f: $R_1 = R_2 = CHCH_2$
g: $R_1 = Me, R_2 = Ph$
h: $R_1 = Et, R_2 = CHCH_2$

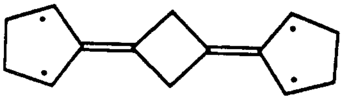
The origin of the triplet ground state preference in **1a**, (and presumably in **1b-h** as well), deserves close inspection, for it may well be a unique phenomenon. In molecules as well as in atoms, in order for triplet ground states to arise, two conditions must be met: The half-filled orbitals must be degenerate or very nearly so, and their overlap must be zero or very small. These are considered to be the primary criteria for the unpairing of spins; the greater the energy difference between the two half-filled orbitals, and/or the greater the overlap, the more the tendency will be seen to pair the electrons in the lower energy orbital (singlet ground state).[9] However, even with degenerate, half-filled orbitals with zero overlap, a triplet ground state may not confidently be expected unless the exchange repulsions between the two radical centers are significant.[7]

Overlap between orbitals containing free electrons in molecules results in the activation of a kind of molecular Pauli principle; mixing of the orbitals favors electron pairing. Exchange repulsions, on the other hand, favor a triplet state. In the case of 1,3-cyclobutanediyl, an odd coincidence occurs, whereby significant through-space overlap is almost exactly compensated by an oppositely signed through-bond overlap (via the CH_2 orbitals of π symmetry), such that the resulting net overlap is extremely small. At the same time, exchange repulsions between the radical centers, separated at a distance of 2.12 A, are quite large. Thus, the conditions which favor a high-spin ground state are fulfilled in this system; the result for **1a** is a calculated triplet preference of 1.7 kcal/mol.[7]

While the high-spin preference in this family of biradicals obviously owes much to serendipity, research in our laboratories indicates that there may be a rather large window within which 1,3-cyclobutanediyls still exhibit triplet ground states. The basic skeleton is very versatile, and appears to be largely indifferent to substitution at the radical centers; there is no evidence as yet of a reversal in the energetic ordering of spin states.

This class of localized, 1,3-biradicals may be uniquely suited to perform in the role described above as a linker unit between intrinsic high-spin fragments. While simultaneously interrupting π conjugation, and thus preserving localized states, they may also be expected to "relay" information concerning spin alignment from one unit to the next, by means of their own substantial exchange repulsions.

It was with these considerations in mind that a model compound was designed in order to test the hypothesis outlined above. The originally conceived target tetraradical, **2**, is particularly appropriate in that it sandwiches the coupler between two units of an extraordinarily stable non-Kekule fragment, the so-called "Berson's TMM", **3**. Trimethylenemethane itself, **4**, has been described as a 1,3-biradical with an extremely effective through-bond coupling unit. When incorporated into a five-membered ring, the strain incurred in the closed shell form causes the planar triplet biradical to be preferred by 10 kcal/mol; the triplet biradical is in turn *ca.* 15 kcal/mol more stable than the bisected singlet. The S-T gap in 2-isopropylidenecyclopentane-1,3-diyl, **5**, which is more relevant to the design of **2**, is also calculated to be approximately 15 kcal/mol.[10] Berson TMM's were thus considered ideal candidates for the intrinsic high-spin units in the test molecule. Any relaxation of the high-spin preference of these fragments incurred by the perturbation to the system should be easily absorbed, given the size of the S-T gap.



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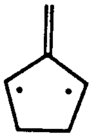

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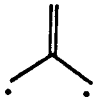

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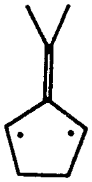

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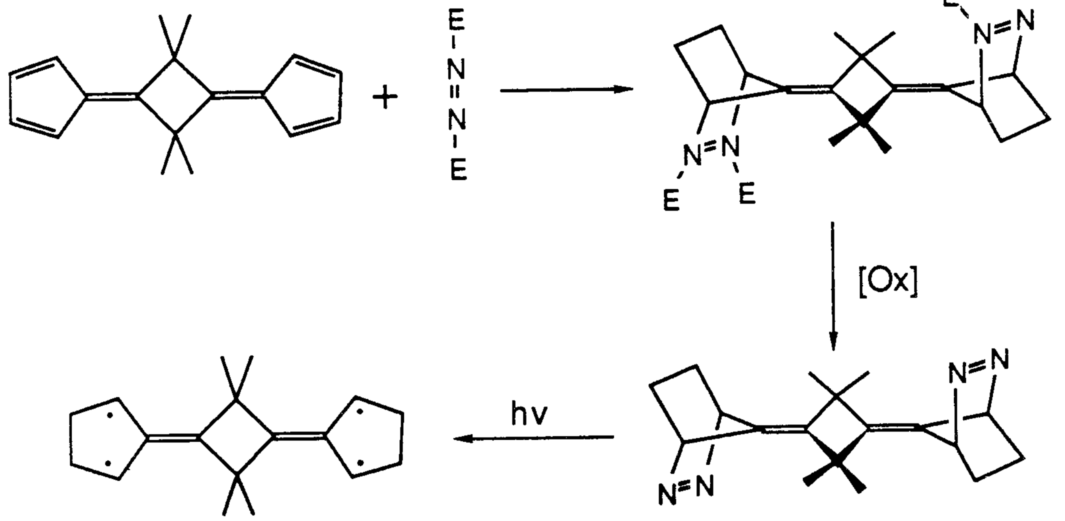
RESULTS AND DISCUSSION

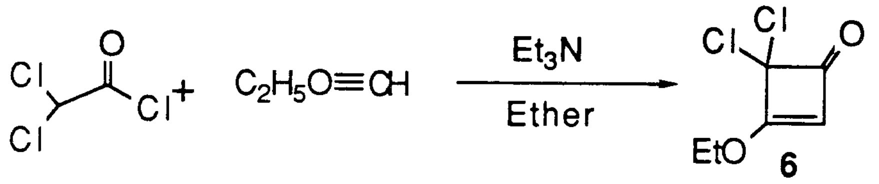
A. SYNTHESIS

While there are many synthetic routes to biradicals, the singular success experienced in our research group in obtaining these structures via photochemical deazetization of appropriate precursor molecules, dictated the obvious strategy.[4g] Scheme 1 illustrates the generalized plan, beginning with the required bisfulvene.

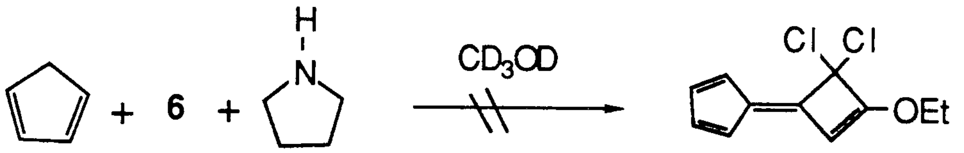
Scheme 1:



The protected derivative 4,4-dichloro-3-ethoxycyclobut-2-en-1-one, **6**, was synthesized by the method shown in Eq. 1[11] for a first attempt at the fulvene synthesis under the Little conditions.[12] The intention, in the event that fulvene was formed, was to then hydrolyze the vinyl ether to the ketone, perform a second fulvene synthesis, and finally reduce off the chlorines with zinc. However, as is often the case with new research, this plan was laid to rest at the first step. Reaction of **6** with cyclopentadiene monomer and pyrrolidine in methanol-d_4 in an NMR tube gave no evidence of incorporation of cyclopentadiene in the NMR spectrum (Eq. 2). Although it was difficult to assign the peaks unambiguously to a particular product, there did appear to be evidence of a possible Michael addition of pyrrolidine to this unsaturated ketone. Similar behavior with α,β-unsaturated ketones was noted in the Little paper in some cases.[11]

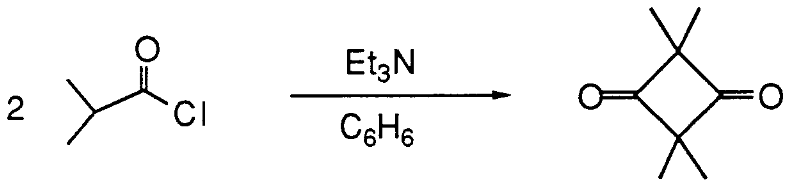


(1)



(2)

A second application of the Little process was attempted using 2,2,4,4-tetramethyl-1,3-cyclobutanedione, **7**, as substrate. This derivative was chosen for a first try in lieu of the parent 1,3-cyclobutanedione due to its ease of synthesis and greater stability. The synthesis of this molecule is shown in Eq. 3.[13] While there is no Michael acceptor unit in this molecule, it suffers from substantial steric congestion at the α positions, a factor which was cautioned against with respect to the Little conditions.[11] The experiment was first attempted in an NMR tube, with methanol-d_6 as solvent. The spectrum clearly revealed a ring-opened product, but surprisingly, in this case the nucleophile was apparently the deuterated methoxide ion (Eq. 4). This was evidenced by the appearance of an isopropyl pattern just above δ 1.0, consisting of a doublet (for H in the iPr group), with a singlet growing up in the center (for D in the iPr group). As the isopropyl group could only arise through ring-opening, it was at first puzzling that no peaks ascribable to the nucleophiles known to be present could be found in the product. This very lack of signals pointed to the deuterated solvent, which, in retrospect, was not very surprising; the sterically hindered approach to the carbonyl probably gave the edge to the smaller methoxide ion.



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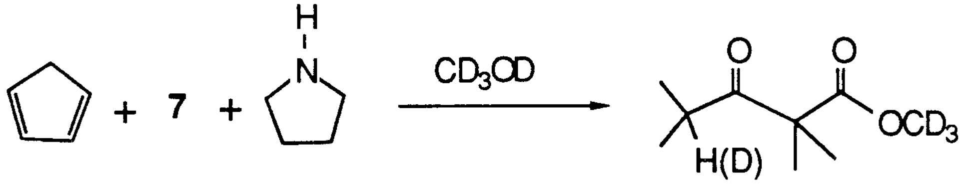
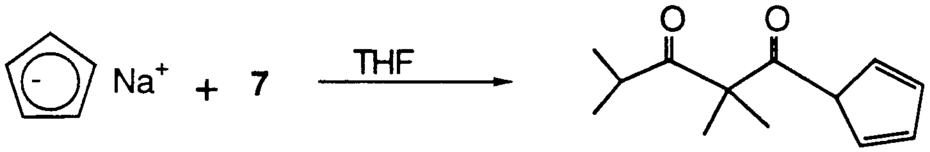
(3)



(4)

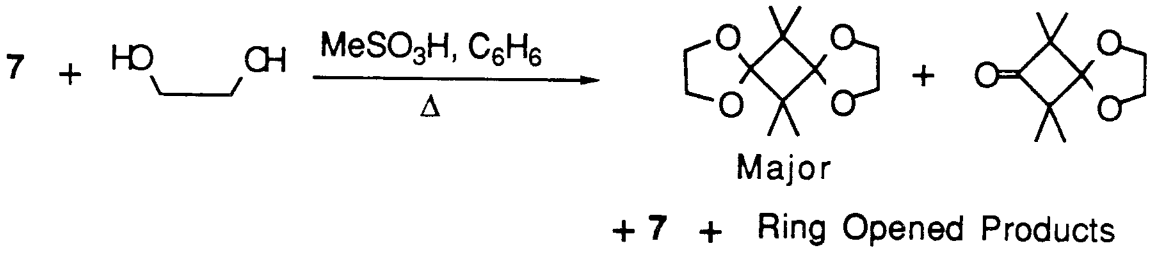
At this point it appeared that the Little fulvene synthesis was contraindicated for the present purposes, in light of the numerous restrictions imposed on the substrates, e.g., no α substituents, no α,β-unsaturation. Attention was therefore turned to other procedures for generating fulvenes.

A second attempt was made to prepare the fulvene of 7, this time using sodium cyclopentadienide as the nucleophile. This reaction was not undertaken naiively, in hopes that the ring would not open under these conditions. Rather, it was run as a test on the steric crowdedness of the carbonyl; if the cyclopentadienyl anion could be made to attack the ketone, in the absence of competing, smaller nucleophiles, then it would be worthwhile protecting the diketone. Otherwise, the tetramethyl substituted derivative would have to be abandoned. As shown in Eq. 5, the result was that the anion did, in fact, open the ring, and this was taken as encouraging evidence that the carbonyl was in fact accessible. Accordingly, efforts to monoprotect the diketone were set in motion.



(5)

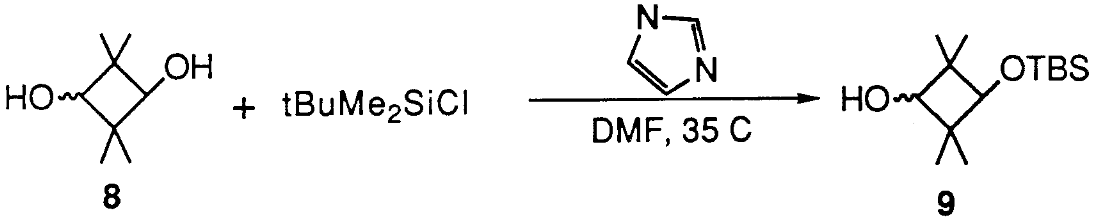
Unfortunately, numerous attempts to procure the monoprotected **7** met with failure. As a typical example, when **7** was permitted to react with 1 eq ethylene glycol and either toluenesulfonic acid or methanesulfonic acid catalyst in refluxing benzene, a preponderance of bisdioxolane was observed in the NMR spectrum of the product mixture, along with small amounts of the monodioxolane, 7, and ring-opened products (Eq. 6). All attempts to isolate the monodioxolane from the other reaction products failed.



(6)

A second attempt was made to protect the diketone using ethanedithiol as the protecting group, with boron trifluoride etherate as catalyst. This noxious procedure left the starting material unchanged.

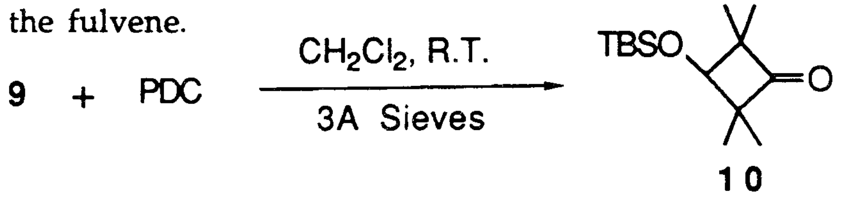
In view of the difficulties encountered in the attempted protection of the diketone, and the inability to use the unprotected compound in the synthesis, other routes were again explored. It was reasoned that if the corresponding diol, (commercially available from Aldrich), could be readily monoprotected, it would be worth the extra oxidation steps in the synthesis. This, in fact, turned out to be the case. When combined with 1.2 eq dimethyl-*tert*-butylsilyl chloride and 2.5 eq imidazole in dimethylformamide solvent,[14] 2,2,4,4-tetramethyl-1,3-cyclobutanediol, **8**, yielded 52% of the purified monoprotected **9** in approximately equal amounts of the *syn* and *anti* isomers (Eq. 7).



(7)

Oxidation of 9 proceeded smoothly using pyridinium dichromate[15a] (PDC, 1.5 eq) as the oxidant, with 3 A sieves (Eq. 8).[15b] This treatment gave a purified yield of 60% of the desired monoprotected ketone, **10**.

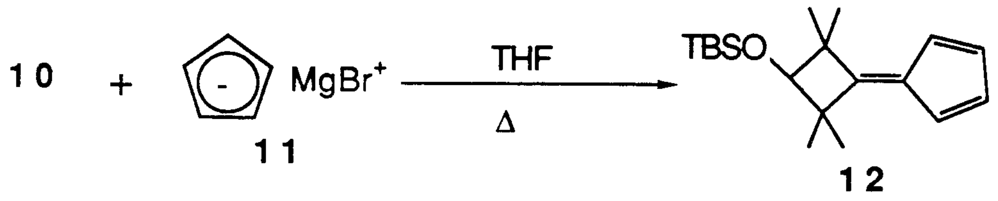
Treatment of the TBS-protected ketone **10** with sodium cyclopentadienide in refluxing THF surprisingly gave no products (Eq. 9). However, as the protected ketone was now available, the problem seemed to be only a matter of finding the right nucleophile and the right conditions which would lead to the fulvene.



(8)

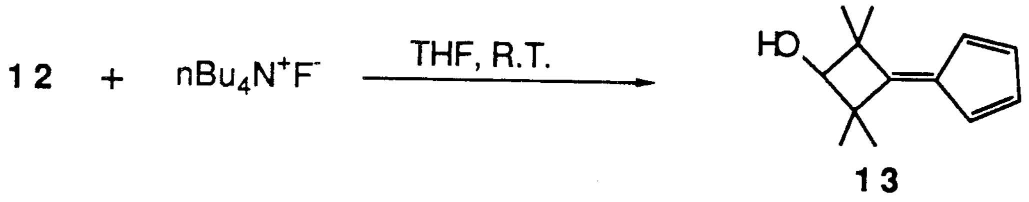
(9)

At this point, the strategy of looking for a "hotter" nucleophile was reexamined. It was reasoned that the problem probably was not in the attacking strength of cyclopentadienyl anion, since its ability to open the ring had already been demonstrated. Therefore, it seemed reasonable to assume that with the help of a good counter ion to interact with the carbonyl oxygen, the fulvene, or at least a cyclopentadienyl adduct, might be within reach. With these considerations in mind, **10** was next subjected to attack by the Grignard reagent, cyclopentadienylmagnesium bromide, **11**,[16] in hopes that the better counter ion ($MgBr^+$ vs. Na^+) would make the difference and lead to the desired product. This hope turned out to be justified, as the reaction of **10** with 1.5 eq of the Grignard reagent in refluxing THF proceeded cleanly *in situ* to the desired fulvene, **12**, in quantitative yield (Eq. 10).

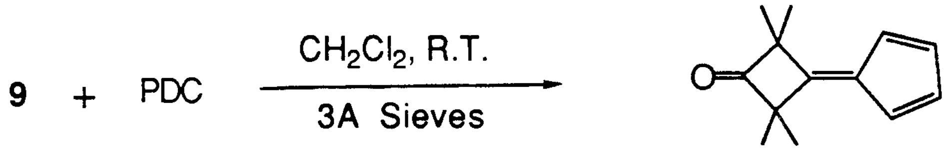


(10)

Deprotection of the TBS-protected fulvene to give the fulvene-alcohol **13** was accomplished in quantitative yield using tetra-*n*-butylammonium fluoride trihydrate as reagent, in THF at room temperature (Eq. 11).[17] Oxidation to the ketone was then effected as before, using PDC as the reagent, and proceeded in yields ranging from 40-60% to the fulvene-ketone, **14** (Eq. 12).



(11)



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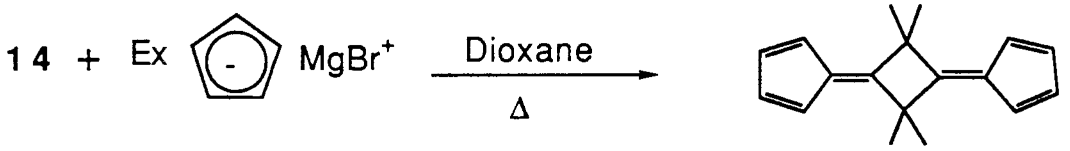
(12)

Although the reaction of **14** with the Grignard reagent **11** was not as facile as it had been the first time with the cyclobutanone **10**, under more forcing conditions, (i.e. refluxing dioxane, large excess of the Grignard), the bisfulvene **15** was ultimately obtained (Eq. 13). However, the yield of the desired product was low (*ca.* 23%). It is not clear whether this low yield was inherent in the reaction conditions, or simply represented poor recovery from the work-up procedures.



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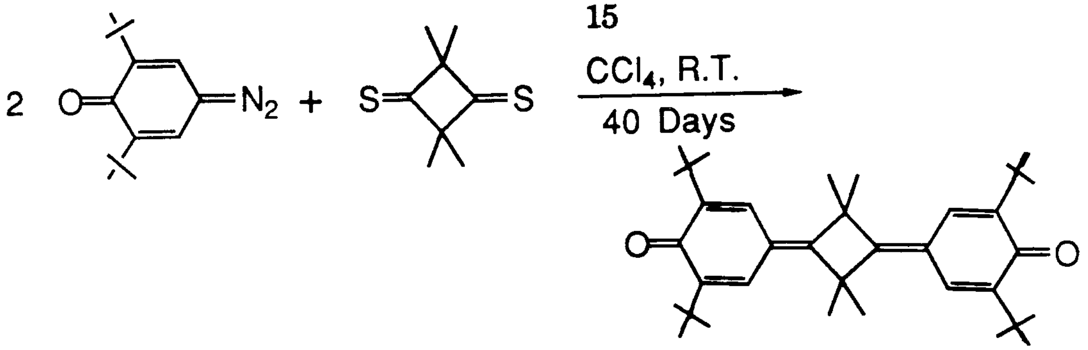
(13)

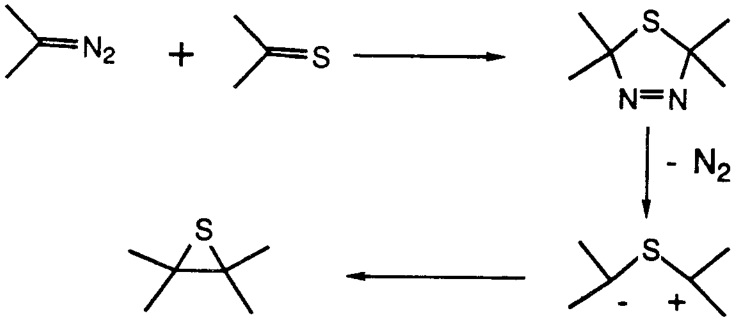
Concurrent with the foregoing work, an alternative route to the bisfulvene **15** was developed, based on work performed by Freund and Hunig with quinone diazides and thioketones.[17] The authors had encountered similar difficulties in obtaining products which were not ring-opened from the reaction of the diketone **7** with nucleophiles, and had therefore sought alternative, non-nucleophilic approaches to quinone methides. Based on chemistry developed by Barton[18] and Kellogg[19], the authors successfully prepared quinone methides by simply allowing the corresponding diazoquinones and thioketones to stir together in the dark for periods ranging from days to months (Eq. 14).



(14)

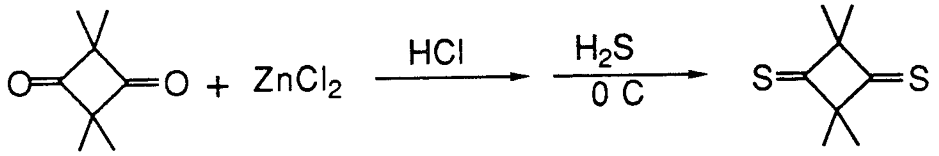
The presumed mechanism of this reaction, a [3+2] cycloaddition, is shown in Scheme 2. The fact that no evolution of dinitrogen was observed prior to addition of the thioketone led to the conclusion that a carbene mechanism was not operative. The reaction is believed to proceed through two intermediates, the first of which is a thiadiazoline. In the work referenced, (as well as in the current research), this species underwent spontaneous loss of dinitrogen under the reaction conditions to give a sulfur ylide, which rearranged to a thiirane (episulfide). In some instances in the referenced work, the thiirane proved labile under the reaction conditions, losing sulfur spontaneously. In other cases, and in the current work, the thiirane was the stable product. Treatment with triphenylphosphine in refluxing benzene then gave the olefinic linkage.

Scheme 2:



This cycloaddition approach appeared especially promising in view of the fact that the authors had already demonstrated that the dithioketone derived from diketone **7** was amenable to this procedure. Moreover, diazocyclopentadiene was a known compound,[20] and indeed had previously been synthesized in our research group.[21]

Accordingly, the dithioketone **16** was prepared by the method of Krapcho *et al*,[22] wherein the diketone **7** is exposed first to hydrogen chloride gas, then to hydrogen sulfide, in the presence of zinc chloride catalyst (Eq. 15). The product precipitates out of the methanol solvent in the form of rose-colored crystals, which can be recrystallized or purified by sublimation. This compound has been prepared twice in the current research; the rather low yield (*ca.* 23%) is attributed to the high volatility of the substrate diketone (H_2S gas is bubbled through the solution for up to 14 hours).



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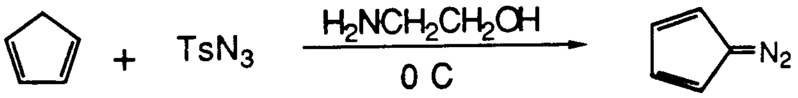
(15)

Diazocyclopentadiene was synthesized according to the procedure of Weil and Cais,[20b] which utilizes p-toluenesulfonyl azide as the diazo source, and ethanolamine as the base/solvent to deprotonate the cyclopentadiene monomer (Eq. 16). The p-toluenesulfonyl azide is easily prepared by simply allowing p-toluenesulfonyl chloride and sodium azide to stir together at room temperature. The crude product **17** was purified by vacuum distillation, or vacuum transferred.



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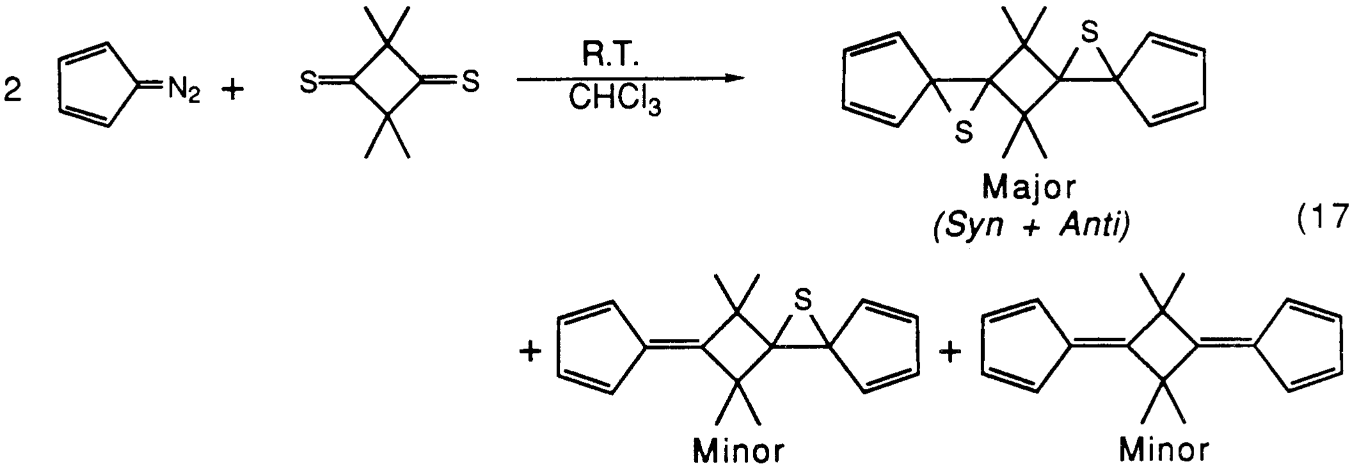
(16)

The reaction of the dithioketone **16** and 2 eq diazocyclopentadiene **17** proceeded agonizingly slowly at room temperature in the dark, in deuterochloroform (Eq. 17).



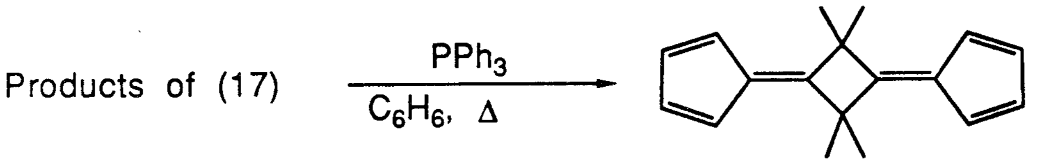
(17)

Progress of the reaction was monitored by 400 MHz NMR. Consumption of the dithioketone **16** cannot be used as a probe to measure reaction completeness, due to the fact that the first addition of diazide is far more facile than the second; similar behavior was noted by Freund and Hunig.[17] Similarly, disappearance of diazocyclopentadiene cannot be used as an indicator, as an excess of the reagent is used. Consequently, the reaction is shut down when a) the concentration of diazocyclopentadiene appears to be remaining constant, and b) the peaks in the NMR assigned to the monothiirane are nearly gone. As noted above, addition of the second diazide is much slower, and of course the rate falls off with time; there is therefore definitely a point of diminishing returns.

This reaction has been performed on three occasions; increasing the number of equivalents of diazocyclopentadiene from 1 to 2, and increasing the concentration (up to neat), resulted in a vast improvement both in reaction time (3 weeks vs. 3 months) and in yield of the desired bisfulvene **15**. While these extremely sluggish reaction times are completely in accord with many of the reaction times noted by Freund and Hunig, further work is clearly required in order to identify factors which will accelerate this process.

Flash chromatography of the crude reaction mixture gave an unresolved mixture of "bis" products which included, as judged from the NMR spectrum, *cis* and *trans* bisthiiranes, and the latter in various stages of elimination to mono- or bisfulvenes. As noted above, the thiirane was by and large stable to the reaction and work-up conditions, so spontaneous desulfurization had not occurred to a great extent.

On the first occasion, the mixture of "bis" products was treated with triphenylphosphine in refluxing benzene for several days, as per Freund and Hunig. Purification by flash chromatography then gave the bisfulvene **15** in the form of very clean, transparent yellow crystals (Eq. 18).



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(18)

On subsequent occasions, it was found that treatment of the crude product with triphenylphosphine at room temperature overnight sufficed to completely desulfurize the thiiranes.

With the crucial hydrocarbon framework now in hand, attention was turned to procuring the urazole precursor to the diazene. Early attempts at obtaining the Diels-Alder adducts of monofulvenes with dienophiles such as 4-methyl-1,2,4-triazoline-3,5-dione (MTAD), and diethylazodicarboxylate (DEAD), had been successful. However, there had been some circumstantial evidence noted at the time that these adducts might undergo retrocycloaddition at or near room temperature. (This first synthetic route, which involved the complete construction of one hydrogenated adduct at a time, with the other alcohol still protected, had to be abandoned when repeated attempts to deprotect the hydrogenated adduct resulted in total decomposition). It was therefore not a complete surprise when **15** was found to undergo both facile cycloadditions as well as *retro*cycloadditions, at room temperature.[23]

This behavior was first noted on reaction of **15** with dimethylazodicarboxylate (DMAD). The reaction proceeded to completion on addition of an excess of DMAD to the bisfulvene in dry ether at room temperaure, as evidenced by the total disappearance of the spot corresponding to **15** by TLC, with concurrent formation of a single product spot at lower R_f. Work-up, (which consists simply of filtration of the crude reaction mixture through basic alumina to remove free DMAD) , was performed immediately. The NMR spectrum ($CDCl_3$) of the resulting *yellow* film revealed no adduct, no DMAD, but all the peaks corresponding to the fulvene. A TLC of the contents of the NMR tube confirmed that the original product spot had disappeared, while the fulvene spot had reappeared. Most of the original bisfulvene was recovered intact from the reaction mixture, indicating that the retrocycloaddition had indeed occurred under the reaction conditions (i.e. in ether), and not just in the more polar NMR solvent. Similar results were obtained with MTAD.

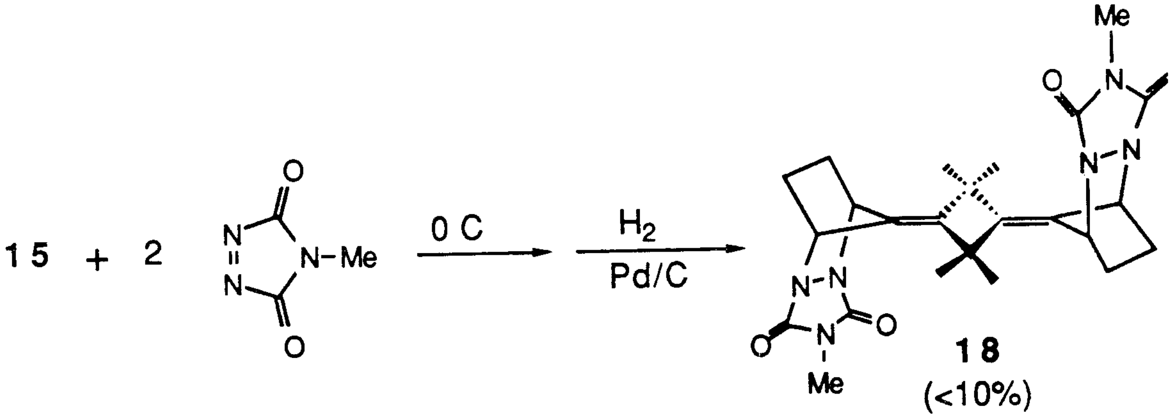
The experiment was repeated in an NMR tube, using PTAD this time, in an effort to observe the retrocycloaddition "in the act". A large excess (*ca.* 3 eq.) of the dienophile was used to insure that the equilibrium would be forced to products initially. A sample of the bisfulvene was dissolved in deuteriochloroform in an NMR tube, and solid PTAD was added in portions. Shaking the tube caused the magenta color (the color of PTAD) of the solution to disappear. This process was repeated until the color persisted. The tube was then plunged in a beaker containing ice water and kept there until its transfer to the spectrometer. In this way, a very clean and diagnostic spectrum of the bis adduct, with *syn* and *anti* isomers both clearly present, was obtained. There were no other peaks other than solvent in the spectrum. After sitting in the probe of the spectrometer for approximately fifteen minutes (T~25 C), a second spectrum was taken, which revealed the onset of significant decomposition. Peaks ascribable to bisfulvene, as well as to other, unidentified decomposition products, were present.

The fact that a clean bis addition was effected, and could apparently be preserved, at low temperature, was encouraging. In the NMR tube experiment, the chlorinated solvent ($CDCl_3$) was probably a factor contributing to the instability of the adduct[24], notwithstanding its tendency to undergo retrocycloaddition. Unfortunately, much time was subsequently squandered on trying to find conditions under which the bisadduct could be catalytically hydrogenated before it underwent the dreaded retro reaction.

Believing that *in situ* catalytic hydrogenation of the crude bisadduct had to be the answer, efforts were focused on "one pot" schemes, and virtually every variable (solvent, concentration, catalyst, temperature, pressure, duration, incantation) was tweaked. One constant which emerged from the data accumulated in these astonishingly irreproducible experiments was the fact that, on the rare occasions when hydrogenated bisurazole was obtained, it was always the *anti* isomer. Even when every fraction from the chromatography column was collected and inspected by 400 MHz NMR, no hydrogenated *syn* adduct was ever seen. Since it was known from the NMR tube reaction between the bisfulvene and PTAD that both isomers are formed, and in approximately equal amounts, it was concluded that the *syn* isomer is much less stable than the *anti*. To date, no conditions have been found under which the *syn* isomer survives hydrogenation.

As all else had more or less failed, this one pot approach was finally called into question. Following procedures established previously in the group, a solution of the bisfulvene in n-hexane was "titrated" with a solution of MTAD in ether until a faint pink color persisted. The reaction mixture was not filtered through alumina; previous results had suggested that the bisadduct was held up on the gel. Instead, the crude reaction mixture was rotary evaporated to give a snow white solid (>100% of the theoretical yield, due to excess MTAD), the NMR of which showed only *syn* and *anti* bisadduct, and MTAD. It was thus established that the unreduced bisadduct was being formed quantitatively and had a measurable lifetime. Although the NMR tube was not left in the spectrometer a while for a "second look", it was noted on this and other occasions that whenever the adduct was dissolved in chlorinated solvents (chloroform or methylene chloride), the initially clear solution took on a yellow tinge. Samples became increasingly yellow with each dissolution in chlorinated solvents.

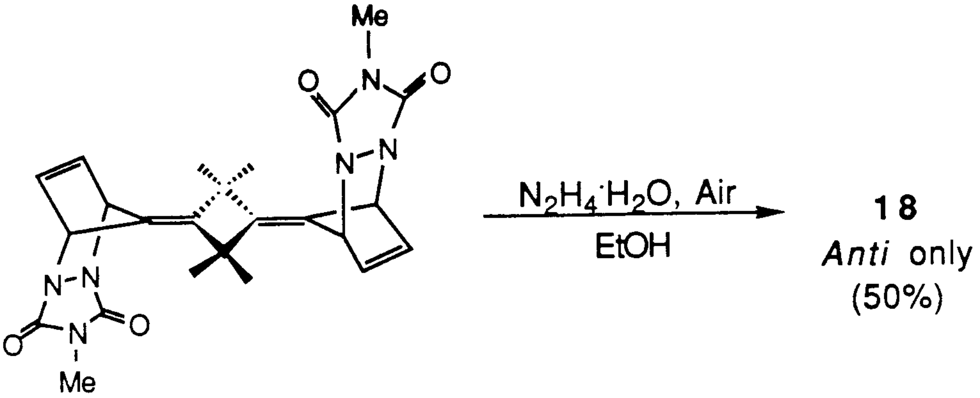
Although the isolation of the adduct was a step in the right direction, the results of attempts to catalytically reduce the endocyclic double bonds were just as capricious as before. Clearly, the hydrogenation step was implicated as the monkey wrench in the system. Again, conditions were adjusted in every conceivable way: Pd/C (two different suppliers), Rh/Al_2O_3 (with and without a trace of acetic acid), Wilkinson's catalyst (*tris*-triphenylphosphine rhodium chloride, a homogeneous approach), as well as a variety of solvents, pressures, and hydrogenation apparatuses were all tried. The typical crude product mixture gave an extremely complex NMR spectrum, a plethora of TLC spots, and *ca.* 10 mg or less of the *anti* bisadduct (Eq. 19). The sea of peaks usually present in the methyl and methylene regions of the spectrum suggested that overhydrogenation (of the exocyclic double bonds) could be a problem; it was difficult to reconcile this interpretation with the fact that olefinic peaks were invariably seen as well.



(19)

In spite of the inefficiency and unreliability of this reaction, eventually enough hydrogenated bisurazole was amassed by this method to enable carrying the synthesis through to the bisdiazene tetraradical precursor. Discussion of the subsequent, relatively trivial steps in the synthesis of the bisdiazene will be deferred for now until after introduction of the method which finally proved highly successful in producing the *anti* reduced bisurazole in quantitative yield.

When air was bubbled overnight through a solution consisting of *syn* and *anti* bisurazole "dissolved" in ethanol, to which had been added an excess of hydrazine hydrate, the *anti* hydrogenated bisurazole was obtained in quantitative yield (Eq. 20). (Since the *syn* isomer of the unreduced bisurazole is highly unstable in solution, it is convenient to think of the final yield as 100% , based on a 50% conversion.)

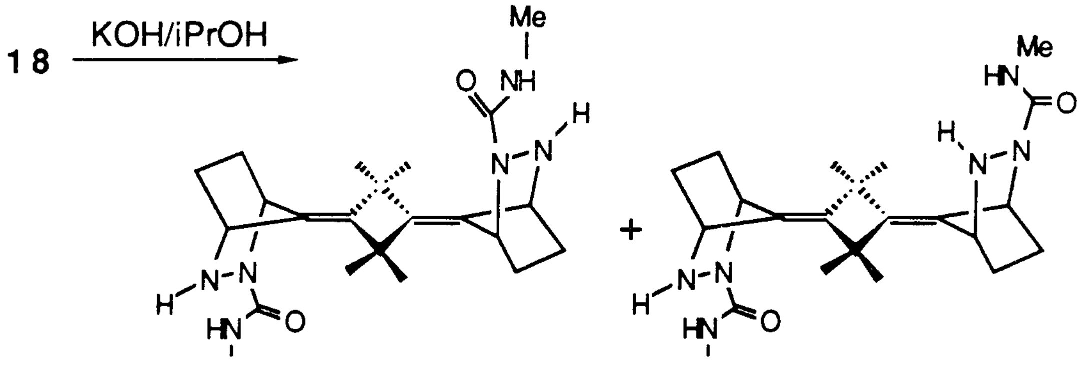


(20)

This reaction was performed, with identical results, on two occasions. Both times the crude product, as revealed by 200 and 400 MHz NMR spectroscopy was remarkably clean, showing product, solvents, a little grease, and very little else. A TLC of the crude product revealed a preponderance of the *anti* hydrogenated bisurazole, with only very minor amounts of side-products.

It's difficult to say exactly why the diimide reduction succeeds admirably for this particular substrate, while the catalytic reaction fails. Others in the group have obtained perfectly satisfactory results in the catalytic hydrogenation of related compounds. (It should be noted, however, that retrocycloaddition of various Diels-Alder adducts has since been observed in several other cases in the group, involving both fulvenes and simple cyclopentenes.) The fact that the *syn* adduct cannot be hydrogenated by either method indicates the extreme instability of that isomer. It may be the case, however, that in the catalytic process, the bis compounds in some way poison the catalysts. Alternatively, perhaps the compound is too sterically hindered to allow efficient adsorption onto the metal surface; the result then would be that the substrate simply stirs in solution, decomposing quickly in the case of the *syn* isomer, and a bit more slowly in the case of the *anti*. The latter conjecture seems less plausible in light of the fact that the NMR spectra do seem to indicate some reduction of the exocyclic double bonds, which are highly encumbered.

With the bisurazole in hand, a basic hydrolysis to the bis-semicarbazide was easily effected along previously established lines, using KOH/i-PrOH at reflux (Eq. 21). The crude product was a yellow solid. The fact that only the *anti* isomer of the bisadduct was available to be used as starting material simplified the resulting product mixture considerably. Given this restriction, there should be two possible isomers formed, the C_i isomer (**19a**), and the C_2 isomer, (**19b**).



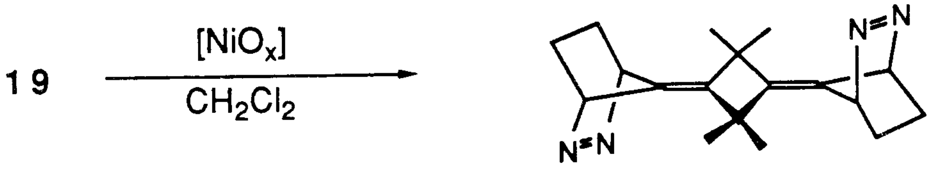
C_i (19a) **C_2 (19b)**

(21)

Monitoring the reaction by TLC (methanol eluant) revealed three distinct spots in the final mixture, a small one at high R_f (UV- active, light blue when developed in Vanillin dip), a large spot also at high R_f (green in Vanillin, characteristic of semicarbazides), and another small spot at lower R_f (green in Vanillin). The crude product was oxidized to the bisdiazene without further purification. It was assumed that the high R_f spot was either the hydrazine derivative of the semicarbazide, or possibly even the azo. Support for the latter assignment was seen when, during the azo preparation, the blue spot appeared to grow in intensity; the lower green spot disappeared altogether, while the upper one seemed to diminish. Overlaying the 400 MHz NMR spectrum of the bis-semicarbazide with the bisurazole confirmed that hydrolysis to the semicarbazide was complete; the N-methyl resonance due to the urazole function was entirely absent. This piece of information was important to insure that neither of the two green spots was due to monosemicarbazide. This then suggests that the two green spots arise from the two possible isomers expected for the bis-semicarbazide, with one of the two isomers being formed preferentially over the other.

The 400 MHz NMR spectrum of the crude bis-semicarbazide does not definitively answer the question of whether there are, indeed, two different isomers present or not. Interestingly, the two isomers are expected to have essentially the same breakdown for numbers and kinds of different protons, with the only difference being in which particular hydrogens are grouped together. As an example, each of the two isomers has two sets of ring methyl protons; in the C_i compound, the transannular methyl groups form a set, while in the C_2 isomer, the geminals are equivalent. The first (and only) difference between these two molecules occurs at a distance five bonds removed from the methyl groups; it should therefore not be surprising if even 400 MHz NMR fails to distinguish between the two compounds. In practice, the NMR shows five distinct singlets in the methyl region, two much smaller than the other three. Similarly, in each isomer, the eight *exo* and *endo* protons on the two ethano bridges form four different sets of two protons each. Again, only the groupings are different. In this case, the NMR shows three multiplets in the methylene portion of the spectrum, two equal in integration, and one a little over double each of the other two. The four bridgehead protons form two groups of two in each isomer. The only difference is whether the equivalent protons are on the same or opposite "sides" of the molecule. In practice, two broad singlets are seen, one at 3.8 ppm and one at 4.65 ppm, which integrate 1:1. The N-methyl semicarbazide protons appear as a doublet at 2.78 ppm. It so happens that the relative integrations between two of the three major methyl singlets and all the other resonances are nearly perfect; it is therefore tentatively concluded either a) that one of the isomers greatly predominates over the other, in which case the third "methyl" singlet is probably water or b) that the two isomers are not differentiated by 400 MHz NMR, except possibly in the methyl region. (The foregoing analysis is predicated on the simplifying assumption that rotation is frozen at the N-CO bond of the semicarbazide functionality.)

Oxidation to the bisdiazene **20** was straightforward, using a substantially relaxed version of the nickel peroxide procedure used routinely in our research group (Eq. 22). The bis-semicarbazide was simply permitted to stir with the oxidant[4g,32]at room temperature under argon in methylene chloride for 15 minutes. The crude product was usually a white powder; however, even when contaminated with yellow material, the desired product was easily extracted by dissolving the film in diethyl ether, from which the bisdiazene readily precipitated.



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(22)

The proton NMR spectrum of the product is fully in accord with expectations for the *anti* isomer of the bisdiazene (see Experimental Section).

More compelling is the characteristic UV spectrum, which clearly indicates the presence of the azo chromophore, $\lambda_{max} = 335$ nm.

As illustrated by the casual reaction conditions, and the fact that the bisdiazene may be stored without undue detriment for long periods at -10 °C, this diazo compound is far sturdier (thermally) than its cyclobutane relatives. For the latter, it is commonly necessary to perform the oxidation at temperatures of ca. -60 °C, and to store the diazene products at -100 °C. (The fact that these latter oxidations can be carried out successfully even at these very low temperatures demonstrates the extraordinary efficiency of the nickel peroxide reaction.)

B. PHOTOLYSIS and EPR SPECTROSCOPY

Having satisfactorily established that the compound in hand was indeed the bisdiazene (uncontaminated with monodiazene), plans were laid for its photolysis under cryogenic conditions in the cavity of an EPR spectrometer. While it was known that others of the so-called "Berson-TMM's" (2-alkylidenecyclopentanediyls) series, **3**, gave stable triplet EPR signals at liquid nitrogen and even higher temperatures,[26] none of these related biradicals contained the saturated moiety, 1,3-cyclobutanediyl. For these latter, localized biradicals, experience told us not to expect to see the *tetraradical*, the species which involves a cyclobutanediyl, at temperatures any higher than 60 K as an upper limit.

At the time when the bisdiazene precursor became available, however, it so happened that the Oxford cryostat was undergoing repairs. Consequently, the bisdiazene was subjected to the usual preparations for photolysis at liquid nitrogen temperatures, but without any real optimism for seeing anything other than the triplet biradical.

The "usual preparations" indicated above consist of the following general procedures: The azo compound is placed in a rigorously cleaned and dried 4 mm or 5 mm quartz EPR tube, into which is vacuum transferred a hydrocarbon solvent, usually 2-methyltetrahydrofuran. The solution is then meticulously degassed through several freeze-pump-thaw cycles, and sealed by means of a vacuum stop-cock under an atmosphere of argon. Samples thus prepared are protected from light and stored at -100 °C.

Encouraged by the exceptional thermal stability of this particular bisdiazene, the compound was simply placed in the EPR tube, and MTHF (*ca.* 300-400 μL, previously vacuum transferred into a dry flask) was added by syringe. It should be noted that this diazene is remarkably insoluble in almost any solvent. Although MTHF appears to be the best of those commonly used as EPR solvents, the major part of azo samples (typically < 5 mg) remains as solid at the bottom of the tube (i.e. a "saturated" solution is exceedingly dilute). Fortunately, EPR spectroscopy is a far more sensitive technique than other forms of spectroscopy; hence, extremely low concentrations of spins may easily be detected.

The sample was freeze-pump-thaw degassed, and transported to the EPR facility in a liquid nitrogen filled finger Dewar flask. In accord with traditional practices in the group, the photolysis was set up so as to irradiate between the wavelengths of 305 and 386 nm, by using a combination of Schott filters in conjunction with the Oriel 100-W mercury-xenon arc lamp (see Experimental Section). During the focussing of the lamp, the sample was not in the cavity. When the lamp had been focussed, the iris was closed, and the sample, still in the finger Dewar, was positioned in the cavity. The "pre-hv" spectrum was completely devoid of signals, as expected.

Throughout the experiment described below, light was allowed to impinge on the sample for various timed intervals, following which the EPR spectrum was recorded with the lamp off. Thus, after an initial irradiation of 15 seconds, the triplet spectrum shown in Figure 1a was observed, and was without hesitation assigned to the monoazobiradical **21**. The zero-field splitting (zfs) parameters, thermal stability, hyperfine coupling constant (hfc, extracted from the half-field transition, *ca.* 14 G), and mode of generation allow us to assign **21** unambiguously as the carrier of the signal, based on comparisons to closely related species.

This is a typical "powder" triplet spectrum, exhibiting the broad lines which arise from the fact that there is an envelope of resonances for each of the three canonical orientations, due to the random distribution of (frozen) orientations in the sample. In addition, there are two possible transitions for a triplet species, corresponding to transitions between the three magnetic sublevels for an S=1 molecule. (These sublevels are inequivalent for a non-spherically symmetric triplet, even in the absence of an external magnetic field, as a result of the dipolar interaction between the two spins; hence the phenomenon known as zero-field splitting.) Thus, given three canonical orientations for each of the two transitions, one would expect to see a maximum of six lines in the first derivative EPR spectrum. These are clearly evident in the $\Delta m_S=1$ portion of the spectrum in Figure 1a, and can best be discerned by counting only the crests of the spectrum.

In rigid matrices, zero field splitting of the three magnetic sublevels is observed, because there is no spherical symmetry in such systems. (Conversely, in fluid media, zfs is *not* observed, because tumbling in solution

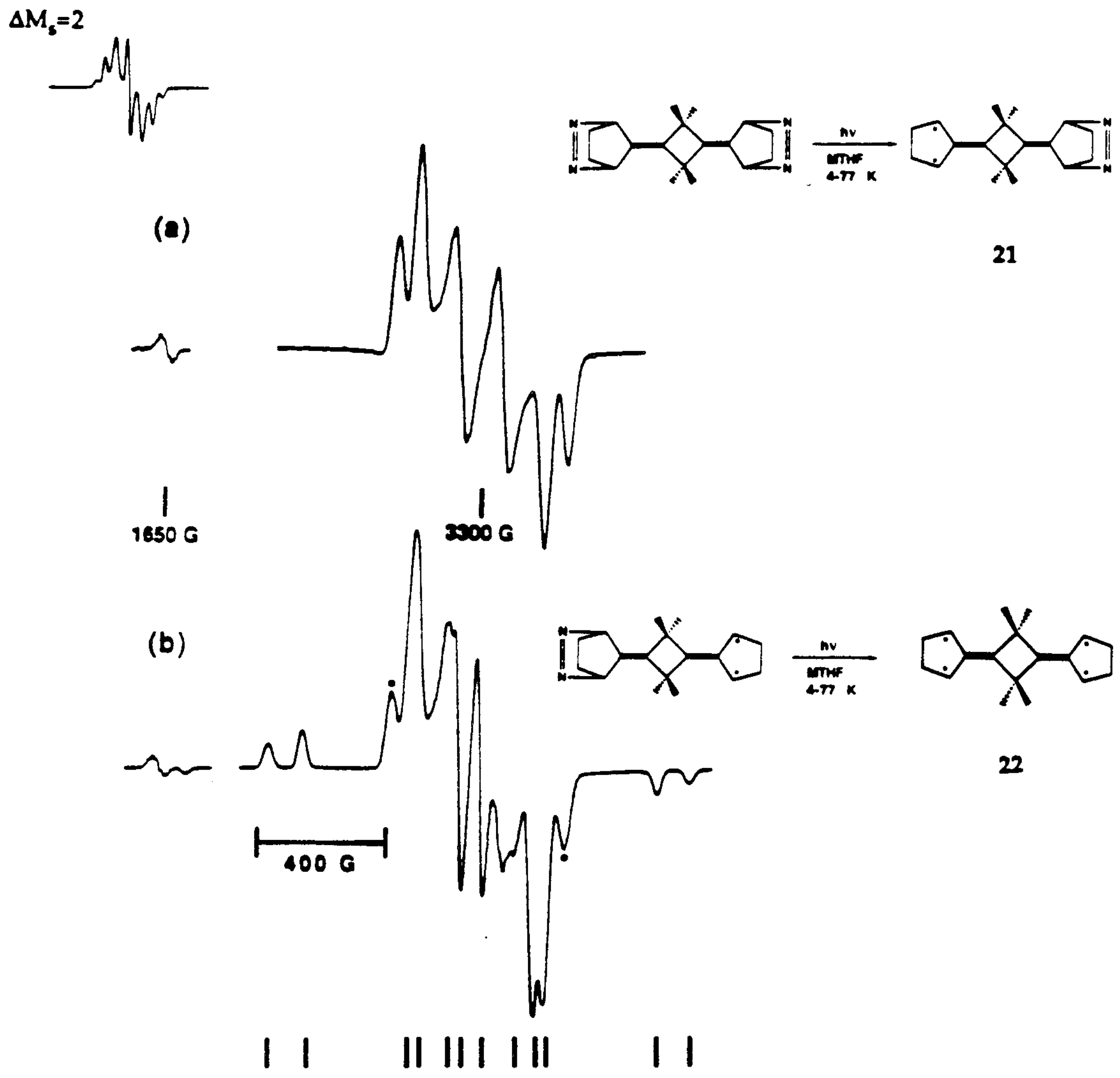


Figure 1. a) Triplet EPR spectrum which results after as little as 15 sec photolysis of **20** in either an MTHF or poly(methylmethacrylate) matrix at temperatures between 3.8-77 K. $|D/hc| = 0.0253$ cm^{-1} and $|E/hc| = 0.0042$ cm^{-1}. *Inset:* $\Delta m_S=2$ transition; hyperfine splitting is *ca.* 14 G. b) Quintet spectrum which results on further irradiation of **20**. $|D/hc| = 0.027$ cm^{-1} and $|E/hc| = 0.0047$ cm^{-1}. Lines marked by asterisks indicate residual triplet **21**. Vertical bars indicate the expected positions of the twelve allowed quintet transitions. Note also the new line in the $\Delta m_S=2$ region.

averages the internal dipolar interactions, effectively imparting a kind of spherical symmetry to the system.) Because the two zero field splitting parameters, D and E, provide important clues to the nature and environment of the absorbing species, matrix isolation EPR spectroscopy is an indispensable tool in the direct observation and characterization of high spin molecules.

By far the more enlightening of the two zfs values is the parameter D (reported as $|D/hc|$). Inversely proportional to the cube of the average interelectron distance (for a triplet), the value of D gives a fairly good estimate of the degree of localization of the spins in the molecule. It is the parameter most frequently invoked to support a particular assignment, especially when used in a comparative sense between closely related species. (In predicting what the relative values of D will be for a given series of molecules, it is important to remember to take into account the magnitudes of the coefficients at the atoms of closest approach for the two electrons.) The D value is easily read off the EPR spectrum; for a triplet spectrum, the distance between the outer two lines is 2D.

Less informative is the parameter $|E/hc|$, referred to simply as E. This value merely indicates whether or not a C_3 or higher axis exists; if it does, E=0, and if not, E takes on some finite value. This point is considered crucial by some investigators for certain applications.[27] Practically speaking, E gives some idea of the degree of planarity of the absorbing species, as it reflects the electron distribution within the X,Y magnetic plane of the molecule.

In practice, the monoazobiradical **21** gives zfs parameters ($|D/hc|=0.0253$ cm^{-1} and $|E/hc|=0.0042$ cm^{-1}) which match well those of the related triplet biradical **23**,[4e] ($|D/hc|=0.0255$ cm^{-1} and $|E/hc|=0.0030$ cm^{-1}), as well as a variety of other 2-alkylidenecyclopentanediyls.[26]

The $\Delta m_s=2$ transition, ("forbidden" or "half-field" transition), is inherently more isotropic than the $\Delta m_s=1$ transitions (i.e. less position dependent). Practically speaking, a more isotropic transition means that the spectral width is narrow; the hyperfine interaction will be on the same order of magnitude as the width of the transition, and the possibility exists for seeing some splitting of the individual lines. Such is the case for the triplet spectrum arising from **21**, and the hyperfine splitting observed (*ca.* 14 G, see inset Figure 1a), concurs with that seen in biradical **23**, (hfs= 13.5 G).

One particularly noteworthy aspect of this triplet biradical is the fact that it apparently survives in a rigid matrix at room temperature. This conclusion was reached upon observing that, when embedded in a poly(methylmethacrylate) matrix, triplet biradical generated by incident sunlight during the transport between buildings (at room temperature) is present in the pre-hv spectrum.

Further irradiation of the sample results in spectra typified by that shown in Figure 1b. In the $\Delta m_s=1$ region of the spectrum, the six lines due to **21** are still in evidence. In addition, there are many new lines, which we assign to the quintet state of the tetraradical **22**, based on the following observations. The new lines, most clearly the two outer pairs (2600, 2710, 3830 and 3935 G), increase upon prolonged photolysis, at the expense of those due to **21**. This suggests that the carrier of the new signal is photochemically derived from **21**, as expected for **22**. (It is interesting to note, in this regard, that generation of the tetraradical is clearly a two-photon process, in contrast to what is observed in the apparent thermal cascade seen when Iwamura and coworkers photolyze their polycarbene precursor molecules.[1c])

The five magnetic sublevels of a quintet species give rise to four allowed transitions; taking into account the sudden jump in the number of absorbing molecules at each of the three canonical orientations, one can expect to see a maximum of twelve lines in the EPR spectrum of a quintet. The positions of these twelve lines may be predicted using a simulation program developed by Seeger, whose Ph.D. dissertation contains an excellent exposition of the intricacies of matrix isolation EPR spectroscopy of organic triplets and quintets.[28] This program, Quintet.For, when fed the D and E values obtained from the EPR spectrum, solves by diagonalizing the 5 X 5 Hamiltonian matrix for a quintet, to give the energies of the five magnetic sublevels. As the microwave energy applied is known (and constant), one simply inserts this vector between adjacent sublevels wherever it fits, to obtain the expected field strengths of the allowed transitions. When applied to the present case, using the quintet zfs values obtained from the spectrum ($|D/hc|=0.027$ cm^{-1} and $|E/hc|=0.0047$ cm^{-1}), the field strengths indicated by hatch marks at the bottom of Figure 1b were obtained;[30] the agreement between the simulated and actual spectra is quite good. (The two outermost peaks in the $\Delta m_S=1$ portion of the spectrum, indicated by asterisks, clearly belong to residual **21**.)

Note that, unlike triplet spectra, quintet spectra typically are *not* symmetrical about the g=2 line (in this case, 3300 G). This is clearly evident in Figure 1b.

The parameter $|D/hc|$ can be readily estimated for quintets by simply averaging the six pairwise interactions between the four unpaired electrons.[28,29] In the present case, the zfs tensors of the subunits are well understood, and so this calculation is straightforward and results in a calculated $|D/hc|$ of 0.0212 cm^{-1}. Certainly, the excellent agreement between theory and experiment must be considered fortuitous to some extent, but the results do indicate that the spectrum observed is quite consistent with structure **22**.

Another feature worth noting in Figure 1b is the appearance of a new signal in the half-field region (*ca.* 1700 G). Theoretically, it is possible to observe Δm_S=2,3 or even 4 transitions in an S=2 (quintet) molecule, depending upon the magnitude of D. In practice, however, it is extremely rare to observe these so-called "forbidden" transitions.[28a] Considering the large number of lines which one could expect from just the $\Delta m_S = 2$ transitions (three such transitions times three canonical orientations for each one), it is not surprising that, unlike the Δm_S=2 signal arising from the triplet, no hyperfine splitting can be resolved.

As noted above, it is *not* the case, in our system, that one photon absorbed by one of the two chromophores of **20** produces a "hot" molecule (**21**) which then spontaneously deazetizes to give **22**.[1c] That ours is a two-photon process is abundantly clear from the time evolution of the EPR spectra. Nor is it the case, as far as we have been able to determine, that manipulating the wavelength of light used to perform the second deazetization of **21** (from the original combination of filters used to produce the biradical **21**), makes any difference whatsoever in the efficiency of this second step. (This latter maneuver was used quite successfully by Seeger to produce his fully delocalized tetraradical.)[28a] Thus, the pure quintet spectrum has so far eluded us, much to our frustration. This is not too surprising, if one considers that in order to completely eradicate all traces of the triplet **21**, it is necessary to find and irradiate every single molecule of **21**, *without* producing any new monoazobiradical simultaneously. Since one is using the same wavelength range of light used to produce **21**, and in the absence of a thermal cascade effect, any hope of achieving a pure quintet spectrum seems counterintuitive. One can only hope to eventually exhaust all the chromophores positioned correctly to absorb, through prolonged irradiation.

It appears, however, from preliminary observations, that a point of diminishing returns is reached after several hours, which may signify that the quintet is photolabile to some extent.

Because it seemed unlikely at this point that a pure quintet spectrum would be obtained by legal means, we opted to take a peek at the digital spectrum which results when the pure triplet is subtracted from a spectrum consisting mostly of quintet, with a little contamination by triplet.[30] The result is shown in Figure 2. (Note that the ubiquitous triplet is still present to a small degree, as evidenced by the two outermost lines in the $\Delta m_S=1$ region.) Allowing for the poor resolution of the digital spectrum, a comparison of the digital with the experimental spectrum (Figure 1b) reveals roughly the same number and positions of lines, qualitatively; only the intensities appear to differ in certain cases. This admittedly crude sketch of the pure quintet still reassures us, to some extent, that the spectra we obtain on prolonged photolysis of **20** are principally that of the quintet, **22**.

An especially intriguing feature of **22** is its thermal stability. All cyclobutanediyls (**1**) prepared to date, including those with radical stabilizing substituents, decay in the 20-55 K range, and are not easily observed at temperatures above *ca.* 60 K. However, **22** is indefinitely (thermally) stable at liquid nitrogen temperatures (77 K), and can be readily generated at this temperature. The origin of this enhanced stability bears further investigation.

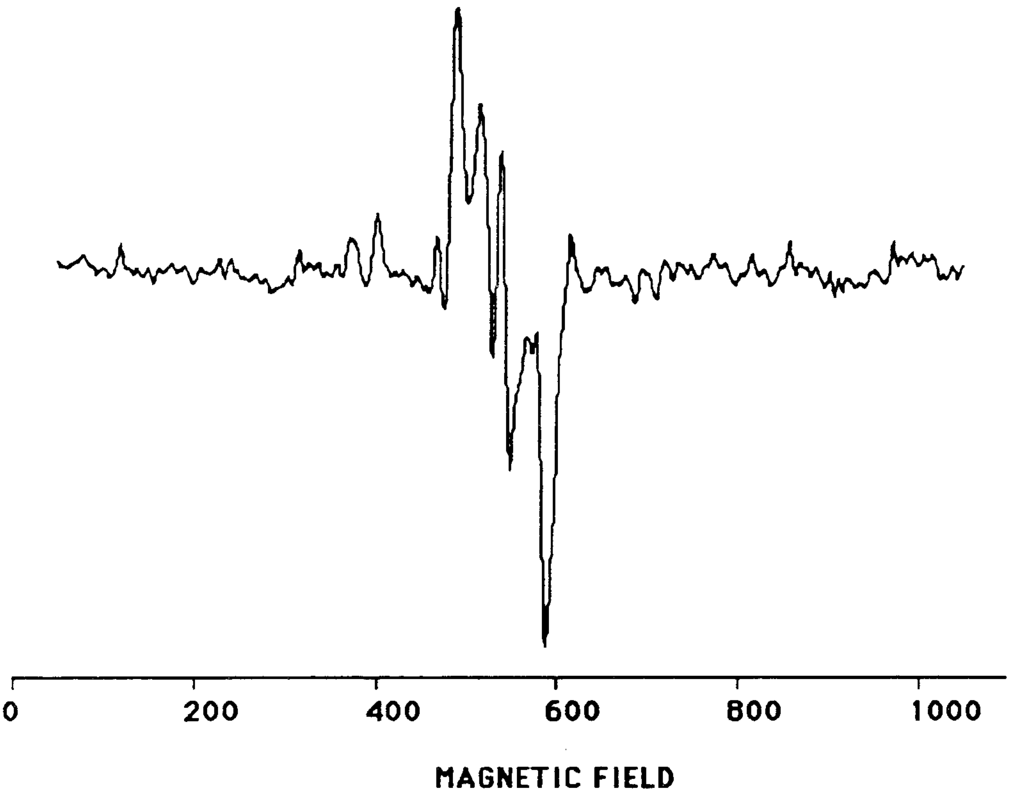


Figure 2. Digital "pure quintet" spectrum obtained by subtracting the pure triplet spectrum from the spectrum obtained after *ca.* 3.5 h photolysis of **20**. Note the two outer lines in the Δm_S=1 region, which belong to residual triplet **21**. The relative scale is correct, but the values are incorrect; the spectrum is centered at 3300 G.

C. ASSIGNMENT of the GROUND STATE

One of the key questions which one would like to address upon observing a photochemically generated EPR-active species, is whether the observed state is the ground, or merely an excited state of the molecule. The assignment is often not a clear-cut proposition, especially when dealing with highly unstable structures. Operationally, the researcher usually relies upon the following three increasingly rigorous criteria in reaching a conclusion: 1) The theoretical basis for the design of the molecule, 2) Empirical evidence (e.g., intensity of the signal at cryogenic temperatures, persistence of the signal in the dark, etc.), and 3) Adherence (or non-adherence) to the Curie Law. Each of these criteria will be discussed in turn, in support of our contention that the quintet state observed is indeed the ground state of tetraradical **22**.

First, design considerations: As outlined in the Introduction, **22** was designed specifically to test the hypothesis that two intrinsic triplets (in this case, the fully delocalized non-Kekule hydrocarbon, 2-alkylidene-1,3-cyclopentanediyl) will be high-spin (ferromagnetically) coupled through the *localized*, ground state triplet biradical, 1,3-cyclobutanediyl. The assertion was based on extensive experience with a family of 1,3-cyclobutanediyls, not one of which (aside from the parent)[8] failed to exhibit a triplet ground state, regardless of the substituents at the radical carbons. Emphasis must be laid on the fact that this project presupposed the high spin ground state of the two units to be coupled; it was not our intention to attempt to align four uncorrelated spins. Because this is true, (i.e. that there is a prior condition on the interacting species that their own spins be individually correlated), it turns out that there are only two possibilities for the energy level diagrams arising from this weak interaction. If the exchange interaction J is positive, ferromagnetic coupling occurs, and a quintet ground state is the result; if J is negative, antiferromagnetic coupling leads to a singlet ground state.[1c] This important simplification of the general case of four electrons in four orbitals greatly aids in the interpretation of some of the empirical observations. For example, since it must be the case that if the observed quintet state is *not* the ground state, then the singlet is, it defies reason to suggest that an intense quintet signal could persist, upon cessation of irradiation, at 3.8 K. (Note that the quintet and singlet states cannot be degenerate, as there is a triplet state between them, unless an exact degeneracy occurs between all three states, an untenable argument.)

The empirical evidence which supports our assignment has been partly alluded to above. Strong quintet signals are obtained at temperatures ranging from 3.8 K to 77 K. As noted above, it is very unlikely that the quintet state would be observed, and especially that its signal would remain intense in the dark at 3.8 K unless it was the ground state of the molecule. Furthermore, it appears that the exchange interaction J is relatively large for this molecule, based on the observation that the shape of the spectrum does not change materially from 3.8 K to 77 K, as would be expected if a thermal equilibrium between a triplet and quintet state existed.

Under ideal conditions, if the observed state is the ground state, then the absorbing species should obey the letter of the Curie Law, which states that IT=C, "intensity of the signal times temperature equals a constant", as manifested by a linear plot of intensity versus reciprocol temperature. Ironically, the Curie Law study, which on the face of it should rank highest for scientific rigor, is seriously undermined by two types of problems. First, there are inherent uncertainties in the experiment, in that it cannot distinguish between the two cases wherein a) the observed state is the ground state, and b) an exact degeneracy occurs between differing spin states. Secondly, there are usually experimental impediments to be dealt with, such as signal saturation at the lowest temperatures, and thermal instability of the absorbing species at the higher end. The latter difficulties often result in a Curie Law study conducted over a narrow temperature range, which naturally affects the significance of the experiment. As might be expected, quintets pose further problems, in that now there are potentially *two* EPR-active species for which one must be on the look-out. In spite of these reservations, a linear Curie plot is considered persuasive, if not unimpeachable evidence for a high-spin ground state.

A plot of the results of our Curie Law study[30] is presented in Figure 3. The signal intensities of the two lowest field lines (in the $\Delta m_S=1$ region) were measured at the temperatures indicated, and plotted versus reciprocol temperature. These peaks were chosen primarily because they are unambiguously due to the quintet alone; unfortunately, the most intense lines of the quintet could not be used because it was impossible to be sure that there was no triplet in them as well. Using the least intense lines runs counter to the usual practices. Furthermore, owing to an anomalous "dip" which often appears at the lower temperatures in the $\Delta m_S=1$ region (for both the triplet and the quintet), and which profoundly alters the baseline, the temperature range for this study was limited to 43.5 K - 77.0 K. Still, the foregoing disclaimers notwithstanding, plots of both peaks versus 1/T are fairly linear. If one disregards the two "Quintet 2" and one "Quintet 1" points which are obviously off the trend, the linearity is actually quite good, in spite of the scatter of the points. Efforts are underway to repeat the experiment under more auspicious conditions (i.e. at a time when the mysterious dip is absent), in order to expand the temperature range.

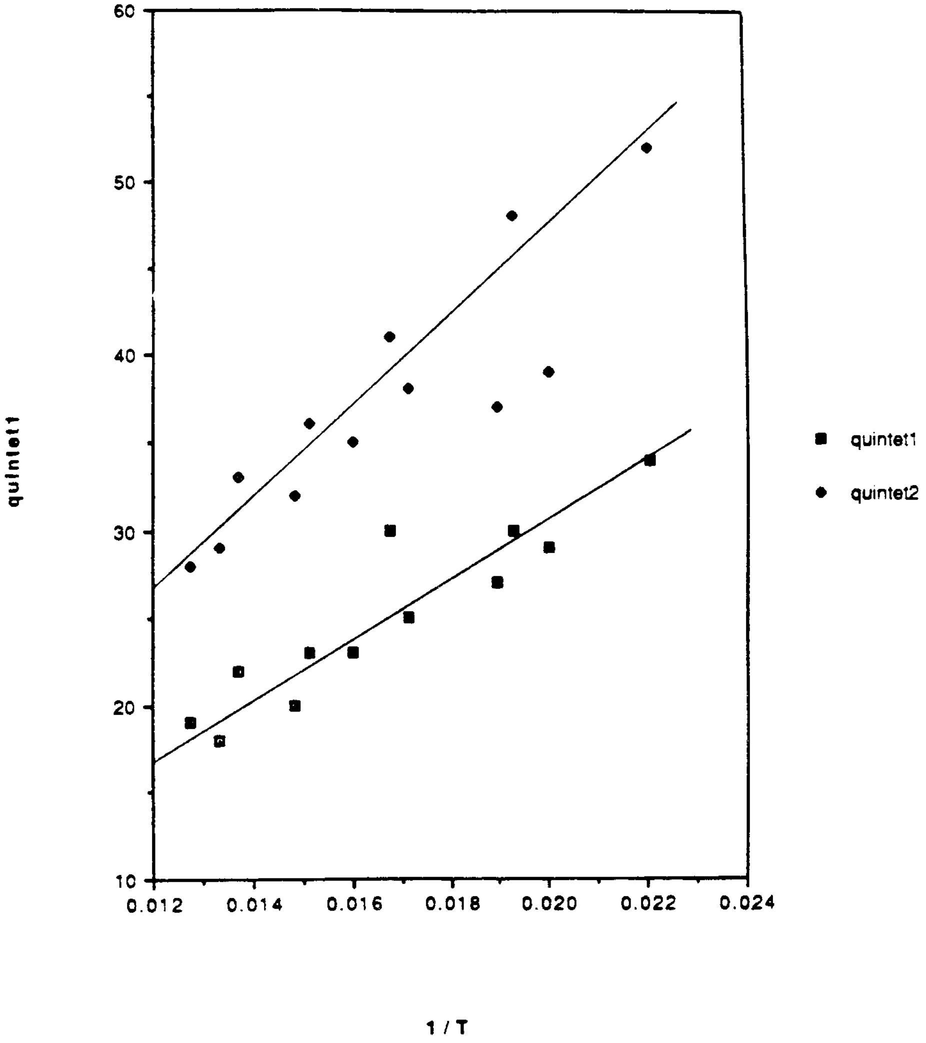


Figure 3. Curie plot obtained from a study of the variation in intensity of the two lowest field lines of the quintet with temperature. "Quintet 1" refers to the outermost line, and "Quintet 2" is the next line upfield. Lines through the two sets of points deliberately reject the three points in the center of the plot, which are clearly artifactual.

CONCLUSIONS and FUTURE WORK

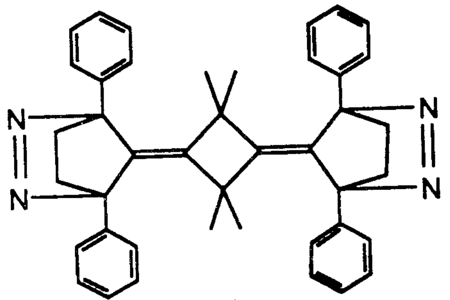
Clearly, the localized biradical, 1,3-cyclobutanediyl, does ferromagnetically couple the two TMM triplets. This is the first rationally designed organic quintet that does not owe its high spin preference to the topology of a delocalized π system. It has long been appreciated that magnetism, unlike conductivity, does not require delocalization, but **22** is the first organic realization of this concept. Further investigations into this and related systems would greatly enrich our current store of knowledge concerning organic ferromagnets, which until now has consisted almost entirely of results gained from the π topology approach.

Specifically, there are several obvious experiments which could summarily answer key questions concerning this system: For example, in light of the fact that no other cyclobutanediyl has exhibited comparable thermal stability, it seems the methyl groups at the intervening carbons of the ring may be implicated as kinetically stabilizing substituents, inhibiting decay to the expected bicyclobutane. This hypothesis could be tested in a variety of experiments, ranging from the synthesis of the parent diazene **20** (without the methyl groups), to a comparison of some of the existing cyclobutanediyls to new analogs substituted with methyl groups.

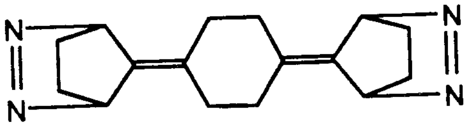
Along slightly different lines, it would be intriguing to test the limits of the ferromagnetic coupling power of the cyclobutane linker by incorporating additional delocalization into the individual TMM's. Intuitively, one might suspect that at some point, the spin density at the 4-ring carbons becomes too small to produce even a weak exchange interaction. Such information is crucial for polymeric applications. One easily envisionable way of testing this notion would be to prepare the tetraphenyl derivative **23**, the analogous bisfulvene of which , may presently be within reach.[31] The tetraradical resulting from the photolysis of **23** would be extremely interesting for other reasons as well. Given the extra radical-stabilizing substituents, it might exhibit even greater thermal stability than **22**. Furthermore, the phenyl groups provide additional chromophores through which to decipher the exact nature of both the monoazobiradical and the tetraradical. One could think of obtaining the UV spectra of both these species through laser flash photolysis techniques. If the monoazobiradical derived from **23** is stable at room temperature in a polymer matrix, as is its parent, **21**, it might be exceptionally convenient to study, without having to resort to laser techniques.

The assertion that it is indeed the cyclobutane moiety which is responsible for the high-spin coupling, and not simply a serendipitous finding, could be greatly reinforced by the preparation of the cyclohexyl linker derivative **24**. (The biradical 1,4-cyclohexanediyl is expected to be a ground state singlet.) The required bisfulvene has already been painlessly synthesized, using the commercially available 1,4-diketone and cyclopentadiene in a straightforward application of the Little fulvene synthesis.[12] It remains only to carry the synthesis forward to the bisdiazene **24**.

Through the promising results of this first test vehicle, an opportunity has been created to explore wholly new avenues in the pursuit of the demystification of the arcane realm of magnetism. Roar on.



23



24

EXPERIMENTAL SECTION

General: ^{1}H Fourier transform NMR spectra were recorded on a Varian XL-200 or JEOL GX-400 spectrometer. ^{13}C Fourier transform NMR spectra were recorded on a JEOL FXQ 90 or JEOL GX-400 spectrometer. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Benzene was distilled from CaH_2 prior to use, except when used as chromatography eluant. Tetrahydrofuran, dioxane, and diethylether were distilled from benzophenone ketyl prior to use. All other solvents were reagent grade and used as purchased, unless otherwise indicated. Column chromatography was performed according to the method of Still,[25] using 230-400 mesh silica gel.

2,2,4,4-Tetramethyl-1,3-cyclobutanedione (7). To a sample of isobutyryl chloride (30.47 g, 0.286 mol, 1.0 eq) in *ca.* 300 mL freshly distilled benzene was added, dropwise, triethylamine (37.03 g, 0.366 mol, 1.3 eq) in 100 mL dry benzene. The mixture was brought to reflux and left to stir under nitrogen for *ca.* 36 h. Triethylamine hydrochloride was removed by filtration, the reaction mixture was washed once with 5% hydrochloric acid, twice with water, and dried over magnesium sulfate. Due to the high volatility of the product, the solvent was removed by azeotropic distillation,using methanol as the second component. When the remaining 10 mLs of methanol were placed in the refrigerator overnight, large off-white crystals precipitated, which were washed with ice cold ethanol. A second crop combined with the first gave a final yield of 9.35 g (46.7%). ^{1}H NMR ($CDCl_3$): δ 1.2 (s).

3-Dimethyl-*tert*-butylsiloxyl-2,2,4,4-tetramethyl-cyclobutanol (9). To 2 mL dry dimethylformamide, stabilized by means of an oil bath at 35 C, were added 2,2,4,4-tetramethyl-1,3-cyclobutanediol (mixture of isomers, 1.0 g, 6.9 mmol, 1.0 eq), dimethyl-*tert*-butylsilyl chloride (1.25 g, 8.3 mmol, 1.2 eq), and imidazole (1.18 g, 17.3 mmol, 2.5 eq). After stirring 15 minutes, the reaction was judged complete by TLC. Appx. 2 mLs water were added to the reaction pot, and the mixture was transferred to a separatory funnel. The organic phase was diluted with *ca.* 5 mLs dichloromethane, removed, washed twice with 5mL portions of water, and dried over magnesium sulfate. Flash chromatography of the crude product, a colorless oil, using 9:1 petroleum ether: ethyl acetate as eluant, gave efficient separation of the mono- and bis- TBS adducts. The mono-TBS product, (R_f 0.32), was a colorless oil (0.93 g, 52%), consisting of approximately equal amounts of *syn* and *anti* isomers. ^{1}H NMR ($CDCl_3$): δ -0.01 (s, 6H), 0.00 (s, 6H), 0.85 (s, 9H), 0.94 (s, 6H), 0.98 (s, 6H), 0.99 (s, 6H), 1.05 (s, 6H), 1.38 (d, 1H), 1.41 (d, 1H), 3.26 (s, 1H), 3.28 (d, 1H), 3.42 (s, 1H), 3.49 (d,1H).

3-Dimethyl-*tert*-butylsiloxyl-2,2,4,4-tetramethylcyclobutanone (10). To 10 mLs distilled dichloromethane were added **9**, (0.490 g, 1.9 mmol, 1.0 eq), pyridinium dichromate (1.07 g, 2.85 mmol, 1.5 eq), and a small quantity of 3A sieves. The mixture was allowed to stir at room temperature under nitrogen for four hours. It was then diluted with an equal volume of diethyl ether, filtered through silica gel, and concentrated by rotary evaporator. Flash chromatography with 1:1 petroleum ether : benzene as eluant gave

0.325 g (67%) of the desired ketone (R_f 0.35) as a white crystalline solid. ^1H NMR ($CDCl_3$): δ -0.10 (s, 6H), 0.75 (s, 9H), 0.89 (s, 6H), 1.0 (s, 6H), 3.63 (s, 1H).

5-[3-Dimethyl-*tert*-butylsiloxyl-2,2,4,4-tetramethylcyclobutylidene]-cyclopentadiene (12). Cyclopentadienyl magnesium bromide[16] (etherate, $M.W._{eff}$ =403 g/mol) was weighed into the reaction flask in a glove box (9.64 g, 24 mmol, 1.54 eq). The reaction flask was removed to a fume hood, 30 mLs of dry tetrahydrofuran were added, and a solution of **10**, (4.0 g, 15.6 mmol, 1.0 eq) in appx. 10 mLs dry THF was added by pipet. The mixture was permitted to stir at reflux 4-5 h. It was then diluted with an equal volume of diethyl ether, washed once with 10 mLs saturated ammonium chloride solution, twice with 10 mL portions of water, and dried over magnesium sulfate. Removal of solvent by rotary evaporator gave 5.04 g (> 100%) of a golden liquid, clean by 400 MHz NMR. ^1H NMR ($CDCl_3$): δ 0.04 (s, 6H), 0.90 (s, 9H), 1.23 (s, 6H), 1.27 (s, 6H), 3.70 (s, 1H), 6.35 (m, 2H), 6.45 (m, 2H).

5-[3-Hydroxy-2,2,4,4-tetramethylcyclobutylidene]-cyclopentadiene (13). Tetra-n-butylammonium fluoride trihydrate (0.360 g, 1.14 mmol, 2.16 eq) was dissolved in *ca.* 5 mLs dry tetrahydrofuran. To this solution was added **12**, (0.160 g, 0.526 mmol, 1.0 eq) and the mixture was left to stir at room temperature overnight. Dilution with an equal portion of diethyl ether, followed by washing with two 3 mL portions of water and drying over magnesium sulfate, gave 105 mg (105%) of the product in the form of light pumpkin-colored crystals. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6H), 1.42 (s, 6H), 3.8 (d, 1H), 6.35 (m, 2H), 6.45 (m, 2H).

5-[3-Oxa-2,2,4,4-tetramethylcyclobutylidene]-cyclopentadiene (14). To a sample of **13** (29 mg, 0.152 mmol, 1.0 eq) in 2-3 mLs dry dichloromethane were added pyridinium dichromate (86.5 mg, 0.23 mmol, 1.5 eq) and a small quantity of 3A sieves. The reaction mixture was allowed to stir at room temperature for 2.5 h. Dilution with diethyl ether and filtration through silica gel gave a yellow solid. Flash chromatography with benzene as eluant gave a clean separation of the product ($R_f = 0.40$) in the form of lemon yellow crystals (21 mg, 73%). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 12H), 6.38 (d, 2H), 6.55 (d, 2H).

1,3-Bis(pentafulvenyl)-2,2,4,4-tetramethylcyclobutane (15). (Grignard Route) Cyclopentadienyl magnesium bromide[16] ($M.W._{eff}$ = 403 g/mol, 311.2 mg, 0.77 mmol, 2.1 eq) was weighed into the reaction flask in the glove box. The flask was then removed to a fume hood, and 2 mL dioxane (purified by distillation from sodium benzophenone ketyl) were added. To this solution was added **14** (70 mg, 0.37 mmol, 1.0 eq), and the mixture was permitted to stir under nitrogen at reflux for 2 h. Dilution with diethyl ether, washing with two 5 mL portions of water, drying over magnesium sulfate, and flash chromatography (4:1 petroleum ether : benzene) gave 19 mg (22%), of the desired product in the form of dirty yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12H), 6.38 (d, 4H), 6.50 (d, 4H).

2,2,4,4-Tetramethyl-1,3,-cyclobutanedithioketone (16). Prepared by the method of Krapcho *et al.*[22] To *ca.* 40 mL methanol (spectrophotometric grade) in a 100 mL 3N flask equipped with thermometer, and large bore needles for gas inlet and outlet, were added **7** (5.0 g, 0.036 mol, 2.0 eq) and zinc chloride, previously purified by refluxing in thionyl chloride, (2.5 g, 0.018 mol, 1.0 eq). A Dewar flask containing an ice water/salt bath was used to bring the temperature of the solution down to -5 C. Admission of a stream of hydrogen chloride gas into the solution caused a sudden and sharp temperature rise to > 60 C, which gradually fell back down to ~ -3 C. Hydrogen chloride was bubbled through the solution for 1 h. During this time, it was noted that the volume of the solution increased by almost 20-30%. The flow of HCl was stopped, and a moderate flow of hydrogen sulfide gas was introduced. The white solution immediately turned yellow, and eventually, red, the color of the product, which precipitated out as it formed. The reaction was permitted to run at -5 - 0 C for *ca.* 9 h. The highly volatile crude product, in the form of dark rose-colored crystals, was filtered from the solution. A second crop combined with the first gave a combined crude yield of 1.38 g (22.5 %). ^{1}H NMR ($CDCL_3$): δ 1.4 (s). mp 121.5-123 C (lit 125-126).

Diazocyclopentadiene (17). Prepared by a modification of the procedure of Weil and Cais.[20b] p-Toluenesulfonyl azide (5.19 g,0.026 mol, 1.0 eq) previously prepared by allowing p-toluenesulfonyl chloride and sodium azide to stir together at room temperature, was pipetted (liquid at room temperature) into a 50 mL wide neck round bottom flask. A Dewar flask containing ice water was fitted around the reaction flask, causing the tosyl azide to solidify. Ethanolamine (1.60 g, 0.026 mol, 1.0 eq) was slowly syringed in, and a thick solution formed. Addition of cyclopentadiene monomer (1.74 g, 0.026 mol, 1.0 eq) caused the immediate formation of orange-red globules. After *ca.* 1 h, the entire "solution" was dark orange-red. In light of poor mixing, the reaction was permitted to "stir" at 0 C for several days. The solid reaction mixture was then transferred to a medium fritted glass funnel and washed repeatedly with pentane until washings were nearly colorless. The filtrate was then washed three times with water, dried for 1 h over magnesium sulfate, and concentrated by rotary evaporator. The resulting orange liquid was stored at -10 C and aliquots were vacuum distilled as needed (0.5 torr, room temperature, collected at -78 C). ^{1}H NMR ($CDCL_3$): δ 6.1 (m, 2H), 6.85 (m, 2H).

1,3-Bis(pentafulvenyl)-2,2,4,4-tetramethylcyclobutane (15) (Cycloaddition Route). To a sample of **16** (400 mg, 2.32 mmol, 1.0 eq) in *ca.* 3 mL deuterochloroform was added **17** (853 mg, 9.28 mmol, 4.0 eq) in *ca.* 2 mL $CDCl_3$. The cherry-red solution was permitted to stir at room temperature in the dark for *ca.* 3 weeks, while progress of reaction was monitored by 400 MHz NMR. The crude reaction mixture was filtered through silica gel (methylene chloride eluant), concentrated, and then purified by flash chromatography (9:1 petroleum ether:benzene). The yellow band collected was an unresolved mixture of "bis" products, consisting mostly of bisthiiranes. This crude product mixture was accordingly treated with triphenylphosphine (2.6 eq, based on M.W. of the bisthiirane) in benzene overnight.. A second flash column, (9:1 petroleum ether:benzene) gave a single yellow product band, isolated and concentrated to give 285 mg (52 %) of **15** in the form of clear yellow crystals. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12H), 6.38 (d, 4H), 6.50 (d, 4H). ^{13}C NMR ($CDCl_3$): δ 30.08, 50.9, 120.2, 131.0, 137.4, 171.8.

1,3-*anti*-Bis(4-methyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]-decane-3,5-dione-7-ylidene)-2,2,4,4-tetramethylcyclobutane (18). To a sample of **15** (100 mg, 0.42 mmol, 1.0

eq) in *ca.* 200 mL hexane was added dropwise a solution of N-methyltriazolinedione[32] (105 mg, 0.92 mmol, 2.2 eq) in *ca.* 100 mL diethyl ether. Completeness of reaction was monitored by the disappearance of the yellow color due to **15**; dropwise addition was continued just until a faint pink color (due to MTAD) persisted. The solution was concentrated by rotary evaporator to give 194 mg of a snow white solid (~100%). ^{1}H NMR ($CDCl_3$): δ 1.19 (s), 1.30 (s), 1.40 (s), 2.95 (s), 5.20 (s), 6.55 (s). The three methyl singlets clearly indicate the presence of both *syn* and *anti* isomers, in approximately equal amounts. Because the crude product was judged to be quite pure based on the TLC, yield, and 400 MHz NMR spectrum, and because the unreduced bisurazole tends to undergo both retrocycloaddition as well as nonspecific decomposition when placed in solution, the product was hydrogenated without further purification. The unsaturated bisurazole was "dissolved" with the help of sonocation in appx. 250 mL ethanol to give a pearly white solution. Hydrazine hydrate, 2-3 mL was added by pipet, and air was bubbled through the solution overnight. The resulting solution appeared clear. Concentration by rotary evaporator yielded a slightly yellow oil, which was redissolved in methylene chloride. The methylene chloride fraction was washed three times with small portions of water until the aqueous fractions were neutral to pH paper. The organic phase was then dried over magnesium sulfate ca. 2 hours, filtered through Celite, and concentrated to yield a white solid contaminated with a little yellow. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 6H), 1.8 (m, 2H), 2.05 (m, 2H), 2.95 (s, 3H), 4.68 (s, 2H). The presence of only one methyl singlet indicates the loss of all of the *syn* isomer of the unsaturated bisurazole.

Hydrolysis of Bisurazole 18 to the Bis-semicarbazide 19. To a sample of **18** (38 mg, 0.081 mmol) in 2-3 mL degassed 2-propanol were added 50-60 mg freshly crushed potassium hydroxide. The solution was then degassed a second time, and left under an atmosphere of argon. The solution was refluxed for appx. 1.5 h. TLC (methanol eluant) revealed total disappearance of the starting material, and three product spots. A small, high R_f spot which is UV-active and develops blue in Vanillin may be the hydrazine product or possibly even the diazene. The next highest R_f spot, which is the major product, develops green in Vanillin, a characteristic color for semicarbazides. The third spot is a minor product at relatively low R_f which also develops green. While it is surmised that the two green spots may be the two expected isomers of the bis-semicarbazide product (see Text, **19a** and **19b**), this has yet to be confirmed by preparative column chromatographic analysis, and cannot be definitively answered from the existing NMR spectra of the crude product. The crude product was carried forward without further purification to the bisdiazene. ^{1}H NMR ($CDCl_3$): δ 1.22 (s), 1.28 (s), 1.35 (s), 1.60 (m), 1.69 (m), 1.98 (m), 2.78 (d), 3.82 (m), 4.65 (m), 6.28 (broad m).

1,3-*anti*-Bis(2,3-diazabicyclo[2.2.1]heptan-7-ylidene)-2,2,4,4-tetramethylcyclobutane (20). To a sample of **19** (50 mg, 0.120 mmol, 1 eq) in methylene chloride was added, at room temperature, 450 mg (1.8 mmol, 15 eq, assuming 4 mmol active oxidant/g) of nickel peroxide.[33] The suspension was permitted to stir at room temperature for *ca.* 30 min, following which it was filtered through Celite and concentrated by rotary evaporator to yield a white solid. On the occasions when the crude product was an oil, purification was easily effected by dissolving the oil in diethyl ether, from which the bisdiazene readily precipitated. ^{1}H NMR ($CDCl_3$): δ 1.05 (m, 1H), 1.23 (s, 3H), 1.62 (m, 1H), 5.25 (s, 1H).

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30. Dr. Rakesh Jain contributed greatly to the project; specifically, Dr. Jain performed the Curie Law experiment, executed the quintet simulation program (Quintet.For), and procured the digitally subtracted quintet spectrum.

31. At the time of this writing, a crude product of the reaction between 1,4-diphenyldiazocyclopentadiene, and the dithioketone **16**, has not yet been purified and characterized. It appears to be mostly monothiirane, but may contain some bisthiirane as well. If so, then it would seem that the reaction time need only be extended in order to obtain reasonable yields of the bis product.

32. David A. Kaisaki was most generous with his supply of MTAD; thanks, Dave.

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