Conformational Effects on High-Spin Organic Molecules

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The ability of m-phenylene to ferromagnetically couple spin-containing substituents that are substantially twisted out of conjugation is investigated. The "bis(TMM)" strategy is employed, in which two triplet TMM biradicals are linked through m-phenylene to produce relatively stable, organic tetraradicals that are characterized by EPR spectroscopy. Under conditions of moderate twisting (4), ferromagnetic coupling is seen, and the tetraradical has a quintet ground state. Severely twisting both TMMs as in 13 disrupts spin communication, and two noninteracting triplets are produced. This is in contrast to other highly twisted m-phenylene derivatives, in which antiferromagnetic coupling has been observed. Surprisingly, severely twisting only one TMM (14) still produces ferromagnetic coupling and a quintet ground state through a spin polarization mechanism analogous to that proposed for 90° twisted ethylene. Several ring-constrained TMMs (17–19) are investigated as models for more nearly planar systems.

Figure 1. Schematic for design of high-spin molecules and materials. The SC is shown as an arrow.

Effect of Nonplanarity (Twisting) on m-phenylene as an FC

Theoretical studies of 2 have focused on the planar structure, (0,0)m-phenylene, as is appropriate for such a simple molecule. However, one expects that twisting the radical centers out of conjugation with the aromatic ring would substantially alter the effectiveness of the FC. Recently, several groups have addressed this issue. In the highly crowded bisnitroxyls 5 and 6, the two spin-containing units are twisted essentially completely out of conjugation, and the biradicals have singlet ground states. This suggests that (90,90)m-phenylene is an antiFC. In contrast, several extremely congested polyaryl derivatives (7) of 2 still show high-spin ground states, despite what must be very substantial amounts of twisting.

Concerning the present systems, computations (see Experimental Section) suggest that even the parent 4 is significantly twisted out of planarity. To investigate this, we prepared the fulvene 8 and determined its X-ray crystal structure. This fulvene shows significant twisting in the crystal, with φ ~ 37°, suggesting
Figure 2. Heisenberg energy level diagrams for the interaction of two triplets described by a single exchange parameter J.

The quintet preference in 4 may be less than in our previous prediction based on a planar structure.

When two triplets are linked through a potential FC, one can expect one of the two state orderings of Figure 2, depending on whether ferromagnetic coupling ($J > 0$) or antiferromagnetic coupling ($J < 0$) occurs. This is simply the well-known result of applying a standard Heisenberg Hamiltonian to a $T + T$ coupling. Previously, we predicted a Q-T gap of 2200 cal/mol for planar 4, based on the calculated S-T gap in 2 and arguments concerning spin density at the carbons attached to the benzene ring. Assuming ferromagnetic coupling scales with orbital overlap, and thus $\cos \phi$, the expected Q-T gap is $\cos(37^\circ) \times 2200 = 1400$ cal/mol, still consistent with our experimental estimate of a gap > 1300 cal/mol.

Our structural calculations also suggest that replacing the methyl groups of 4 with tert-butyl groups would completely twist the m-phenylene ring out of conjugation with the TMMs. This is supported by the X-ray crystal structure of 9, which shows the phenyl and fulvene planes nearly perpendicular ($\phi \sim 87^\circ$). For further corroboration, we compared the EPR zero-field splitting (zfs) $D$ values (Figure 3, Table I) for TMMs 10 and 11 (prepared by photolysis of standard diazene precursors). Since $D$ is a sensitive probe of the average interelectron separation in a triplet, it is a good indicator of the extent to which the phenyl rings of 10 and 11 delocalize the TMM spins. As expected, the $D$ value for 11 is greater than that for 10 (Table I). In fact, $D(11)$ is nearly equal to that for the dimethyl compound 12 (Table I), confirming a negligible amount of phenyl delocalization in 11.

Table I: Zero-Field Splitting Parameters for Triplet TMMs

| TMM | $D$/cal/mol, cm$^{-1}$ | $|E|$/cal/mol, cm$^{-1}$ |
|-----|------------------------|-------------------------|
| 10  | 0.0195$^a$             | 0.00173$^a$             |
| 11  | 0.0241                 | 0.00406                 |
| 12  | 0.0256$^c$             | 0.0034$^c$              |
| 17  | 0.0196                 | 0.00270                 |
| 18  | 0.0186                 | 0.00128                 |
| 19  | 0.0169$^b$             | 0.00160$^b$             |

$^a$ Determined from the EPR spectra observed after photolysis of the corresponding diazene at 77 K in MTHF. All spectra are well simulated using standard methods. Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. J. Am. Chem. Soc. 1976, 98, 5725-5726.

Photolysis of the bisdiazene 13(N$_2$)$_2$ gives rise to a triplet TMM EPR signal identical to that of 11. The $\Delta m = 1$ signal consistently grows in with first-order kinetics, and the spectral shape remains the same even after prolonged photolysis and cooling to 4.4 K. The $\Delta m = 2$ region is also identical to that of 11, and a Curie plot of its intensity is linear from 10 to 70 K. We have a great deal of experience with the bis(TMM) approach, and we are confident that under these conditions a significant number of precursor molecules have had both N$_2$ units expelled to produce tetraradical 13. We conclude that 13 consists of two noninteracting triplet subunits within the same molecule. One could argue that 13 is simply EPR-silent, because it has a singlet ground state or because it reacts with itself to give a low-spin product. However, under such circumstances the triplet EPR signal would grow in and then decay on extended photolysis, as we have seen previously in another bis(TMM) molecule built around an
antiFC. Thus, in the present context, (90,90)m-phenylene is neither an FC nor an antiFC, at least at temperatures ≥ 4.4 K. Instead, it merely insulates two spin-containing units from one another, allowing them to act independently.

This is in sharp contrast to the previously mentioned bisnitroxyls 5 and 6, in which (90,90)m-phenylene acts as an antiFC. While we have no simple rationalization for this dichotomy, we note that nitroxyl is an unusual spin-containing unit, which has a significant spin–orbit coupling term. This may contribute to the behavior seen in 5 and 6. Another bis(triplet) tetraradical has been reported in which an ethylene unit serves as the spacer. If (0,0)m-phenylene is a good FC and (90,90)m-phenylene is neither an FC nor an antiFC, what is (90,90)m-phenylene? The bis(TMM) approach offers a straightforward means of answering this question using tetraradical which contains both a methyl-substituted and a tert-butyl-substituted TMM. The bisdiazene (14(N)2) was prepared. Brief photolysis gives a signal that clearly arises from a 1:1 mixture of the singly denitrogenated triplet TMM monodiazenes 15 and 16 (Figure 4a,b). Note that the computed spectrum of Figure 4b is not a fitted simulation. Rather, it is a predicted spectrum obtained with no adjustments by simply summing the experimental spectra for 10 and 11 in a 1:1 ratio. This modularity of design constitutes another advantage of the bis(TMM) approach.

Extended photolysis of 14(N)2 (Figure 4c,d) leads to a familiar sequence in which dramatic changes occur, especially in the middle of the spectrum. We assign the final spectrum as due to the quintet state of 14, based on its strong resemblance to the signal observed for the quintet ground state of 4 (Figure 4e) and several related structures. At present we consider it likely that the quintet we observe is the ground state of 14, since the signal is intense at temperatures as low as 4.5 K. We note that these spectra are somewhat featureless, and it is possible that they do not represent pure quintets but contain some contribution from

![Figure 4](image-url)  
**Figure 4.** (a) 1 spectrum observed after brief photolysis (5 min) of 14(N)2 at 77 K in MTHF. (b) Predicted spectrum obtained by adding the experimental spectra of 10 and 11 (Figure 3a and 3b) in a 1:1 mole ratio. (c) 1 spectrum observed after photolyzing 14(N)2 for 9.5 h at 30 K in propylene glycol, annealing at 135 K, and cooling to 11.8 K. (d) Sample in (c) warmed to 135 K. The changes with temperature are reversible. (e) Experimental spectrum of quintet 4 (ref 4).

A rationalization for the quintet ground state in 14 can be developed with reference to Figure 5. We view 14 as two orthogonal triplet subunits, one similar to 10 and the other similar to 11, interacting to produce a quintet state. The delocalized 10-like TMM communicates with the relatively localized 11-like TMM through the a–b bond, a connection that resembles perpendicular D14 ethylene. Calculations predict that twisted ethylene has a singlet ground state due to spin polarization effects. Thus, perpendicular ethylene is an antiFC, but in this case a center of negative spin density (a) is antiferromagnetically coupled to one of positive spin density (b). This produces a net alignment of the positive spin densities and thus overall ferromagnetic coupling (Figure 5).

We can use the twisted ethylene model to predict the Q–T gap in 14. The calculated S–T gap in perpendicular ethylene is ~2 kcal/mol, and since the S–T gap in a biradical is 2J, J14 = ~1 kcal/mol. The J for 14(J14) is related to J<sub>eth</sub> by a straightforward way. J14 should be positive because the spin densities at the joined carbons a and b are of opposite sign (Figure 5). Thus, perpendicular ethylene is an antiFC, but in this case a center of negative spin density (a) is antiferromagnetically coupled to one of positive spin density (b). This produces a net alignment of the positive spin densities and thus overall ferromagnetic coupling (Figure 5).

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may be a useful strategy, especially with spin-containing units that contain large spin polarizations and thus large negative spin densities.

**Constrained Systems**

Given the substantial twisting in 11/13 and the nontrivial twisting presumably present in 10/4, we felt it would be interesting to investigate structures designed to be more nearly planar. This may be valuable for future designs that want to make optimal use of the m-phenylene FC. Therefore, we have prepared the constrained-ring TMMs 17, 18, and 19, for comparison to 10 and 11.

![Diagram of TMM structures](image)

Model calculations (see Experimental Section) on these biradicals and UV data for the analogous fulvenes indicate that 17 is essentially planar, 18 less so, and that 19 and 10 have roughly the same twist. As indicated earlier, 11 likely has the phenyl ring essentially perpendicular to the TMM plane. One complication is that not only may the phenyl ring twist out of the plane of the TMM, but the TMM itself may twist internally, complicating detailed analysis of such structures. To first order, however, based on the simple trend above, we expected the D value of 17 to be small, that of 18 somewhat larger, those of 19 and 10 larger still, and that of 11 to be the largest.

The EPR spectra of biradical 17 are straightforward (Figure 3). Photolysis of the diazene precursor at 77 K in MTHF gives a $\Delta m_1 = 1$ spectrum with $|D/|hc = 0.0196, |E/|hc = 0.00270$ cm$^{-1}$. The spectrum is unchanged at 3.8 K. The $\Delta m_2 = 2$ spectrum (not shown) is a nonet, $a_H 12.2$ G, due to hyperfine coupling to eight hydrogens, two $\alpha$ and six $\beta$. We have previously shown that in such TMMs the magnitudes of the $\alpha$ and $\beta$ hyperfine splittings are very similar, and pleasingly simple splitting patterns are observed.

The EPR spectra of biradical 18 are also straightforward (Figure 3). Photolysis of the diazene precursor at 77 K in MTHF gives a $\Delta m_1 = 1$ spectrum with $|D/|hc = 0.0186, |E/|hc = 0.00128$ cm$^{-1}$. A nearly identical spectrum is observed in propylene glycol. The $\Delta m_2 = 2$ spectrum is a nonet, $a_H 11.25$ G. Photolysis of the diazene at 4.0 K gives the same $\Delta m_1 = 1$ and $\Delta m_2 = 2$ spectra as at 77 K.

We have observed interesting temperature-dependent behavior in biradical 19 (Figure 6). Photolysis of the diazene precursor at 77 K in MTHF gives a $\Delta m_1 = 1$ spectrum with $|D/|hc = 0.0169, |E/|hc = 0.00160$ cm$^{-1}$. A nearly identical spectrum is observed in propylene glycol. Photolysis at 4.0 or 50.0 K gives a similar but slightly different spectrum, with $|D/|hc = 0.0165, |E/|hc = 0.00214$ cm$^{-1}$. Warming the sample to 77 K causes the high-temperature spectrum to be irreversibly restored.

Significant temperature effects are also observed in the $\Delta m_2 = 2$ region (Figure 7). Photolysis at 77 K gives a nonet, $a_H 11.6$ G. Photolysis at 4.0 or 50.0 K gives an octet with $a_H 11.6$ G. Warming the sample to 75.0 K gives the nonet. Thus, the low-temperature spectra indicate hyperfine coupling to only seven hydrogens, but the high-temperature spectra indicate coupling to eight. The octet to nonet conversion is irreversible and occurs at approximately the same temperature as the irreversible changes in the $\Delta m_2 = 1$ spectrum. This strongly suggests that all the changes are due to the same process, most likely a conformational change in the TMM after nitrogen loss from the diazene precursor.

![Diagram of TMM structures](image)

The irreversible changes in the $\Delta m_2 = 2$ region can be simulated by considering each spectrum to be a weighted sum of the limiting octet and nonet spectra (Figure 7). When done properly, this constitutes an example of the "distribution slicing" technique that we have previously employed to analyze kinetics in frozen matrices. Figure 8 shows the results of fitting the data of Figure 7 to a collection of matrix sites that display a Gaussian distribution of Arrhenius activation energies. The width of the Gaussian ($\sigma$) is 0.6 kcal/mol, in excellent agreement with our previous analysis of frozen solvent systems. If we assume log $A = 13$ (Table II), the center of the Gaussian, and hence the most probable rate, corresponds to $E_A = 4.6$ kcal/mol.

Although we cannot unambiguously identify the process that corresponds to these activation parameters, a reasonable candidate is a conformational change involving the cyclohexene ring.
The irreversible decrease in $D$ on warming is explained if the TMM is initially formed in a conformation with the phenyl ring substantially twisted from the plane of the TMM. Warming the sample apparently allows the phenyl and TMM to become more nearly coplanar. The changes in the $\Delta m_2 = 2$ region are reasonably explained by considering the effect of temperature on the methyl group. The nonet observed at low temperatures implies eight coupled hydrogens—six from the TMM and two from the CH$_3$. The $\Delta m_2 = 2$ septet observed for 10-D$_3$ confirms this assignment. Apparently, at low temperatures the CH$_3$ is frozen in a conformation with one C–H bond in the plane of the TMM, as is typical for vinylic methyl groups. On warming the sample, CH$_3$ rotation becomes rapid and a complex spectrum is observed.

One surprising feature of the series 17–19 is the trend in zfs $D$ values (Table I), which runs completely contrary to our initial expectations based on presumed degree of planarity and thus biradical delocalization. Apparently, some other factor is influencing the $D$ values, and we propose that this may be twisting of the TMM unit itself. Our calculations (see Experimental Section) do suggest substantial twisting of the TMMs (and the analogous fulvenes) due to steric interactions of the sort shown in 19a, and the extent of twisting follows the series 19 > 18 > 17. It is difficult to predict how such twisting will influence a TMM $D$ value, but if our interpretation is correct, it apparently leads to a decrease in $D$. In light of this, it is dangerous to interpret the surprising result that $D(10) \approx D(17)$.

Conclusions

Using the bis(TMM) strategy, the influence of twisting on the effectiveness of $m$-phenylene as a ferromagnetic coupling unit has been evaluated. Under conditions of modest twisting (4), $m$-phenylene is still an effective FC. Completely twisting both spin-containing units out of conjugation with the $m$-phenylene (13) leads to no interactions at all, and the SCs act independently.
and degassed with several freezepumpthaw cycles. A liquid and vacuum transferred from sodium benzophenone ketyl) or 2-methyltetrahydrofuran (MTHF, refluxed over CaH2, distilled, then frozen).

An Oxford Instruments ESR-900 liquid helium cryostat was used for variable-temperature experiments (3.8-135 K). Samples were photolyzed in the EPR cavity with the filtered, focused output of a 500-W Hg arc lamp. Lamps, housings, and HRMS determinations were performed at the University of California, Riverside. UV spectra were taken using a Beckman DU-640 spectrometer. A range of peak positions indicates a complex conjugation. The ring-constrained systems 17-19 display complex conformational behaviors, and their D values seem to reflect effects other than just degree of coplanarity between the TMM and the aromatic ring.

**Experimental Section**

**General.** Reactions were performed under an argon atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH2. Reported yields refer to material dried to constant weight under vacuum, typically 50 mTorr. Flash chromatography was on 230-400 mesh silica gel with the solvent indicated. All NMR shifts are reported as δ ppm downfield from TMS. 1H NMR was at 300 MHz in CDCl3, and 13C NMR was at 75 MHz in CDCl3 using a GE QE-300 spectrometer. A range of peak positions indicates a multiplet of poorly resolved lines. IR spectra were recorded on a Perkin Elmer 1600 series instrument. MS refers to a 70-eV effective MW of about 400. A representative fulvene preparation is given below. An alternate oxidation with CuCl2 is also given.

**General Route to Diazenes.** The diazene precursors for all the TMMs were synthesized via similar routes. The ketone starting material was converted to the fulvene, which was reacted with dimethyl azodicarboxylate (DMAD) and reduced to the bicsarbarmate. This was hydrolyzed and oxidized to the diazene (see figure below). All diazenes are stored at -20 °C in CH2Cl2 solution.

![Figure 10. Dm = 2 spectra observed after photolysis of 10(N2) at 4.2 K in MTHF. The changes with temperature are reversible.](image)

Interestingly, having one SC in plane and one SC completely out of plane as in 14 apparently still leads to ferromagnetic coupling. We propose a novel mechanism in which antiferromagnetic coupling between a center of negative spin density and a center of positive spin density leads to overall ferromagnetic coupling. The anti FC involved resembles the singlet biradical 90° twisted ethylene.

Several TMM biradicals have been studied as potential probes of conformational effects. The bulky substituent in 11 leads to a relatively large D value, consistent with the predicted loss of conjugation. The ring-constrained systems 17-19 display complex conformational behaviors, and their D values seem to reflect effects other than just degree of coplanarity between the TMM and the aromatic ring.

**1,3-Dipivaloylbenezene (13k).** A 1.28-g portion of 1,3-dicyanobenzene (10.0 mmol) was dissolved in 40 mL of dry THF in a flame-dried flask under argon and then 11.5 mL of 2.0 M t-BuMgCl/ether (23.0 mmol, 2.3 equiv) was added, followed immediately by 36 mg (0.40 mmol, 0.04 equiv) of CuCN.27 The mixture was rapidly heated to reflux. After 21 h, the solution was cooled to room temperature and carefully quenched with 5 mL of water followed by 30 mL of 15% sulfuric acid. The biphasic mixture was stirred at room temperature for 22 h and then 25 mL of ether was added and the layers shaken and separated. The aqueous layer was extracted with 25 mL of ether. The organic extracts were combined and concentrated to give 0.94 g (38%) of 9.4% analytically pure material. An analytical sample was recrystallized from ethanol/water, long white needles, mp 48-50 °C. 1H NMR δ 8.04 (dt, J = 1.8, <1 Hz, 1H), 7.80 (dd, J = 7.8, 1.8 Hz, 2H), 7.26 (dt, J = 7.8, <1 Hz, 1H), 1.37 (s, 18H). 13C NMR δ 208.27, 138.19, 130.04, 127.3, 44.19, 27.88. IR (NaCl plate, cm⁻¹) 1677, 1650 cm⁻¹. MS M+ 246 (1), 190 (23), 189 (100), 57 (48). HRMS calcd for C16H22O2: 246.1620, found 246.1618. Anal. Calcd for C16H22O2: C 78.01, H 9.00, found C 77.96, H 9.10.

**Ketal from 3-Acetylbenzonitrile.** A 250-g portion of 3-acetylbenzonitrile (17.22 mmol) was dissolved in 50 mL of benzene. Ethylene glycol (9.6 mL, 10 equiv) and 330 mg of p-TsOH.H2O (1.73 mmol, 0.1 equiv) were added. The mixture was heated to reflux using a Dean-Stark trap to remove water. After 5 h of reflux the cooled solution was quenched with 25 mL of each of water and saturated aqueous (sadt. aq.) NaCl. The layers were shaken and separated, and the aqueous layer was extracted with 2 × 25 mL of benzene. The organic extracts were combined and rotovaporated, giving a quantitative yield of a colorless solid. 1H NMR δ 7.81 (t, J = 1.7 Hz, 1H), 7.75 (dt, J = 7.8, 1.5 Hz, 1H), 7.60 (dt, J = 7.5, 1.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 4.08...
(m, 2H), 3.78 (m, 2H), 1.64 (m, 3H). 13C NMR δ 144.98, 131.33, 129.69, 128.97, 128.90, 118.57, 112.09, 107.73, 64.47, 27.28. MS [M-CH3]+ 174 (100), 130 (87), 102 (46).

3-Acetylpyrrolophenone (14k). A 3.34-g portion of cyano ketal (17.7 mmol) was dissolved in 50 mL of dry THF in a flame-dried flask under argon and 13.2 mL of 2.0 M t-BuMgCl/ether (26.4 mmol, 1.5 equiv) was added, followed immediately by 41 mg (0.06 mmol, 0.02 equiv) of CuCN.27 The mixture was rapidly heat to reflux. After 2.5 h, the solution was cooled to room temperature and carefully quenched with 20 mL of water and then 50 mL of 15% sulfuric acid. The biphasic mixture was stirred for 13 h at room temperature. The layers were shaken and separated, and the aqueous layer was extracted with 2 × 50 mL of ether. The organic layers were combined, dried (MgSO4), and filtered through silica (5:1 hexanes:ethyl acetate) providing 3.25 g (85%) of a colorless oil. 1H NMR δ 8.28 (d, J = <0.5, 1.8 Hz, 1H), 8.06 (dd, J = 7.5, 1.8, 1.2 Hz, 1H), 7.89 (d, J = 7.5, 1.8, 1.2 Hz, 1H), 7.53 (dt, J = <0.5, 7.5 Hz, 1H), 2.64 (s, 3H), 1.37 (s, 9H). 13C NMR δ 208.12, 197.04, 138.69, 136.69, 131.87, 130.20, 127.27, 127.39, 44.03, 27.70, 26.43. IR (NaCl plate, film) 1685 cm⁻¹. MS M⁺ 204 (1), 143 (35), 142 (100), 57 (38). HRMS calcd for C16H16O2: 204.1150, found 204.1153.

Representative Preparation of Fulvenes from Ketones and CpMgBr: 6-(p-Methoxyphenyl)-6-methylfulvene (8).28 A 1.00-g (6.67 mmol) portion of p-methoxyacetophenone and 8.0 g of CpMgBr (3 equiv) were refluxed in 50 mL of dry THF under argon. After 3.5 h, the solution was quenched into 50 mL of satd. aq. NaHCl and 10 mL of water. The layers were shaken and separated, and the aqueous layer was extracted with 25 mL of ether. The organic layers were combined, dried (MgSO4), and filtered. The residue was chromatographed (1% ether/hexanes) to provide 1.00 g (84%) of an orange solid, mp 65.5–66.5 °C (97%) of an orange oil. 1H NMR δ 7.52 (m, 2H), 6.80 (d, J = 5.4, 1.8 Hz, 1H), 6.55 (d, J = 5.4, 2.1, 1.2 Hz, 1H), 6.36 (d, J = 5.4, 2.1, 1.2 Hz, 1H), 1.31 (s, 9H). MS M⁺ 198 (100), 183 (97). HRMS calcd for C16H16O: 194.1096, found 194.1096.

Conformation and High-Spin Organic Molecules

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Fulvene 19f-Dg. Prepared as for 19f from α-tetralone-Dg,1H NMR identical to that of 19f, except methylene peaks replaced by peaks at 2.83 and 1.96 ppm (each t, J = 6.3 Hz, 2H). 13C NMR identical to that of 19f, except methylene peaks replaced by singlets at 29.46, 23.08 ppm and quintet at 30.12 ppm, JcD = 19.7 Hz. MS M+ 196 (100), 180 (56), 167 (55). HRMS calcd for C13H22D3O: 196.1221, found 196.1215.

DMAD Addition and Diimide Reduction: General Procedure. 10r. A 0.685-g portion of fulvene 10f (4.07 mmol) and 0.595 g of DMAD (4.07 mmol, 1.0 equiv) were stirred in 25 mL of dry CH2Cl2 under argon. (For some compounds, as noted, the unreduced DMAD adduct was isolated by chromatography at this point. We have found, however, that immediate reduction of the adduct without isolation is generally more efficient.) After 1 h, the solution was cooled in an ice-water bath, and 1.98 g of PADC (10.19 mmol, 2.5 equiv) was added. A solution of 1.2 mL of acetic acid (21.0 mmol, 5.2 equiv) in 5 mL of CH2Cl2 was added dropwise over 20 min. The mixture was stirred as the flask was allowed to warm to room temperature. Typically the reaction with PADC was allowed to stir overnight before workup. The mixture was quenched with 20 mL of water. The layers were separated. The aqueous layer was extracted with 25 mL each of water and CH2Cl2 with gentle shaking, and the layers were shaken and separated, and the aqueous layer was extracted with 25 mL of CH2Cl2. The organic layers were combined, dried (K2CO3), filtered, and rotary evaporated. The residue was chromatographed (2:1 hexanes:ethyl acetate) to provide 1.018 g (97%) of a white foamy solid. 1H NMR δ 7.3-7.2 (m, 1H), 6.90 (m, 2H), 6.55 (m, 1H), 5.41-5.15 (br m, 4H), 3.75 (m, 12H), 1.97 (br m, 4H), 1.72 (br m, 4H), 1.15 (m, 18H). 13C NMR δ 158.3, 157.0, 140.38, 140.05, 139.93, 139.87, 138.97, 134.76, 134.72, 134.60, 126.62 (br m), 62.1 (br m), 61.5 (br m), 58.9 (br m), 53.3 (br m), 36.05, 35.94, 31.05, 30.82, 26.72 (br m). DEI-MS M+ 638 (8), 538 (38), 537 (100), 375 (32). HRMS calcd for C21H124N6O8: 638.3316, found 638.3316.

14a. From 0.590 g of bisfulvene 1f (1.96 mmol) was isolated by chromatography (2:1 to 1.2 hexanes:ethyl acetate) 455 mg (39%) of a yellow oil which did not solidify. 1H NMR δ 7.4-4.2 (m, 12H), 3.9-3.6 (m, 12H), 2.0 (m, 3H), 1.12 (s, 9H). 13C NMR δ 158.9 (br), 143.7-125.5 (m), 65.9 (br), 65.3 (br), 54.8-52.4 (m), 50.57.

14r. From 0.455 g of 14u (0.768 mmol) was isolated 403 mg (88%) of a pale-yellow foamy solid. 1H NMR δ 7.28 (m, 1H), 7.13 (m, 1H), 6.88 (m, 1H), 6.81 (m, 1H), 5.49-4.43 (br m, 4H), 3.80 (m, 12H), 2.12 (2s, δ 2.6 Hz, to 3H), 2.2-1.4 (br m, 8H). 13C NMR δ 158.5, 157.2, 140.7, 139.02, 135.44, 135.28, 134.92, 127.76, 127.67, 127.47, 127.13, 127.1 (br), 126.99, 125.63, 124.72, 61.9 (br), 49.1 (br), 53.0 (br m), 36.02, 31.01, 26.16 (br m), 20.1 (br). DEI-MS M+ 596 (20), 496 (31), 495 (100), 333 (40). HRMS calcd for C13H10N2O6: 596.2846, found 596.2855.

17r. From 0.306 g of fulvene 17f (1.84 mmol) was isolated by chromatography (3:2 hexanes:ethyl acetate) 416 mg (72%) of a yellow foamy solid. 1H NMR δ 7.23 (m, 4H), 5.38-4.42 (br m, 2H), 4.03-3.35 (m, 8H), 2.36-1.49 (br m, 4H). 13C NMR δ 144.6-119.2 (m), 59.59 (br), 53.25 (m), 36.75, 28.33 (v br), 26.78 (br). MS M+ 314 (50), 167 (94), 166 (100), 165 (87), 59 (100). HRMS calcd for C17H16N2O4: 314.1267, found 314.1275.

18r. From 0.578 g of fulvene 18f (3.21 mmol) was isolated by chromatography (2:1 to 1.2 hexanes:ethyl acetate) 442 mg (42%) of an off-white foamy solid. 1H NMR δ 7.80-7.06 (m, 4H), 5.74-4.57 (m, 2H), 4.00-3.37 (m, 6H), 3.15-2.56 (m, 4H), 2.36-1.45 (m, 4H). 13C NMR δ 147.9-122.8 (m, 60.87 (br), 57.74 (br), 53.38 (br), 30.00, 29.9, 27.17 (v br), 20 eV EI-MS M+ 328 (4), 180 (100). HRMS calcd for C17H18N2O4: 328.1423, found 328.1408.

19r. From 0.685 g of fulvene 19f (3.53 mmol) was isolated by chromatography (2:1 hexanes:ethyl acetate) 800 mg (66%) of a sticky pale-orange solid. 1H NMR δ 7.18 (m, 4H), 5.70-4.55 (m, 2H), 3.77 (m, 6H), 3.05-2.30 (m, 4H), 2.30-1.44 (m, 6H). 13C NMR δ 138.8-125.6 (m, 59.36 (br), 53.14 (br), 29.25, 29.11, 26.90 (v br), 23.77. 20 eV EI-MS M+ 342 (4), 194 (100). HRMS calcd for C19H20D2N2O4: 342.1580, found 342.1563.

Representative Diazone Preparation Using NiO, Oxidant: Diazene 10N2. A 0.218-g portion of 10r (0.689 mmol) and 673 mg of powdered 87% KOH (1 equiv) were degassed 3 times on the vacuum line and purged for 10 min with argon. Then 20 mL of degassed isopropyl alcohol (30 min of argon bubbling) was added via cannula, and the mixture was stirred and heated to reflux for 90 min. The mixture was cooled to room temperature, and 0.87 g of NaHCO3 (15 equiv) was added. The mixture was stirred for 1 h at room temperature, and the solvent was pumped off overnight. The brown residue was partitioned between 25 mL each of water and CH2Cl2 with gentle shaking, and the layers were separated. The aqueous layer was extracted with 25 mL of CH2Cl2. The organic layers were combined, dried (K2CO3), filtered, and cooled in an ice-water bath. A 1.1-g portion of NiO2 was added, and the mixture was stirred at 0°C in the dark for 1 h. The mixture was filtered through Celite and rotary-evaporated to provide 80 mg (58%) of a pale-yellow film. 1H NMR δ 7.32 (m, 3H), 7.12 (m, 2H), 5.50 (d, δ = 2.7 Hz, 1H), 5.27 (d, δ = 2.7 Hz, 1H), 2.00 (s, 3H), 1.75 (m, 2H), 1.16 (m, 2H). 13C NMR δ 141.48, 140.59, 128.11, 127.31, 127.24, 124.89, 74.52, 64.89, 21.28, 21.17, 19.77. UV λmax (CH2Cl2) 297, 342 (sh) nm.
**TABLE III: MM2-Calculated Lowest Energy Structures of Phenyl-Substituted Fulvenes**

<table>
<thead>
<tr>
<th>Fulvene</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_4$</th>
<th>$d_1$ (Å)</th>
<th>$d_2$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Fulvene 1]</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.604</td>
<td>1.472</td>
</tr>
<tr>
<td>![Fulvene 2]</td>
<td>19.6</td>
<td>17.1</td>
<td>3.0</td>
<td>2.3</td>
<td>3.6</td>
<td>2.131</td>
</tr>
<tr>
<td>![Fulvene 3]</td>
<td>41.3</td>
<td>39.2</td>
<td>4.5</td>
<td>4.5</td>
<td>6.4</td>
<td>2.322</td>
</tr>
<tr>
<td>![Fulvene 4]</td>
<td>71.1</td>
<td>70.5</td>
<td>1.7</td>
<td>0.9</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>![Fulvene 5]</td>
<td>70.2</td>
<td>69.6</td>
<td>1.7</td>
<td>1.0</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>![Fulvene 6]</td>
<td>90.0</td>
<td>89.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*All values of $\phi$ (degrees) are reported as deviations from 0° or 180°, whichever was closer.  Two approximately equal H-H distances were found.  MM2 as implemented in MacroModel version 3.5a was used.

**Diazene 10(N$_2$)$_2$D$_2$**. This compound was prepared as for 10(N$_2$).  H NMR was identical to that of 10(N$_2$), except no singlet at 2.00 ppm.  $^{13}$C NMR was identical to that of 10(N$_2$), except no singlet at 19.77 ppm. The septet for the CD$_3$ carbon was observed but poorly resolved from baseline noise.

**Representative Diazene Preparation Using CuCl$_2$ Oxidant:**

**Diazene 11(N$_2$)$_2$**. A 0.292-g portion of 11r (0.815 mmol) and 787 mg of powdered 87% KOH (15 equiv) were degassed 3 times on the vacuum line and purged for 10 min with argon. Then 25 mL of degassed isopropyl alcohol (30 min of argon bubbling) was added via cannula and the mixture stirred and heated to reflux for 90 min. The mixture was cooled to room temperature and quenched with 20 mL of cold water. The solution was acidified to pH ≤ 2 with 1.0 mL of concentrated HCl and adjusted to pH ~ 6.0 with 3 N NH$_4$OH. The pale-yellow solution was treated dropwise with 2.2 mL of satd. aq. CuCl$_2$, giving a dark-brown solution. After 30 min, the pH was adjusted to ~5 with 3 N NH$_4$OH, producing a light-brown precipitate. This was suction filtered (30-mL medium fritted funnel) and rinsed with 50 mL of 3 N NH$_4$OH, giving a blue filtrate. The retained yellow solid was rinsed with 25 mL of CH$_2$Cl$_2$, giving a pale-yellow solution of the diazene. This was chromatographed (1:1 hexanes:ethyl acetate), although this step appears not to increase the purity of the diazene significantly and may be skipped.  H NMR δ 7.27 (m, 1H), 7.04 (m, 1H), 6.84 (m, 1H), 6.62 (m, 1H), 5.84 (m, 1H), 5.51 (m, 1H), 5.22 (m, 1H), 4.55 (m, 1H), 2.01 and 1.99 (each s, total 3H), 1.88-1.40 (br m, 4H), 1.34-0.81 (br m, 4H), 1.12-1.08 (m, total 19H). 13C NMR δ 141.8 (m), 140.58-140.37 (m), 139.95, 127.76-127.28 (m), 74.43, 73.81, 73.65, 72.53, 36.25, 31.09, 31.36-21.11 (m), 20.64, 20.43. UV $\lambda_{max}$ (CH$_2$Cl$_2$) 340 nm.

**TABLE IV: AM1-Calculated Lowest Energy Structures of Phenyl-Substituted Fulvenes**

<table>
<thead>
<tr>
<th>Fulvene</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>$\phi_4$</th>
<th>$d_1$ (Å)</th>
<th>$d_2$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Fulvene 1]</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.627</td>
<td>1.472</td>
</tr>
<tr>
<td>![Fulvene 2]</td>
<td>0.1</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>1.908</td>
</tr>
<tr>
<td>![Fulvene 3]</td>
<td>35.9</td>
<td>34.9</td>
<td>5.5</td>
<td>5.8</td>
<td>3.9</td>
<td>7.4</td>
</tr>
<tr>
<td>![Fulvene 4]</td>
<td>49.6</td>
<td>48.5</td>
<td>2.3</td>
<td>2.1</td>
<td>1.2</td>
<td>3.2</td>
</tr>
<tr>
<td>![Fulvene 5]</td>
<td>48.0</td>
<td>46.8</td>
<td>2.8</td>
<td>2.5</td>
<td>1.7</td>
<td>3.2</td>
</tr>
<tr>
<td>![Fulvene 6]</td>
<td>89.6</td>
<td>89.9</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>![Fulvene 7]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All values of $\phi$ (degrees) are reported as deviations from 0° or 180°, whichever was closer.  The minimization began from a structure with $\phi_1, \phi_2 \sim 75^\circ$.  Convergence criterion was set to 0.001 kcal/mol.  The minimization began from a structure with $\phi_1, \phi_2 \sim 73^\circ$.  Two approximately equal H-H distances were found.  The MM2-minimized structures were used to start the minimization, except where indicated.  MOPAC as implemented in InsightII version 2.1.2 (BioSym) was used with the following parameters: BFGS minimization type, line minimizer off, PRECISE keyword activated, kcal/mol convergence criterion. Frequency calculations showed that all structures are true minima; all elements of the diagonalized force constant matrix were positive.
TABLE V: AM1-Calculated Lowest Energy Structures of Phenyl-Substituted TMMs

<table>
<thead>
<tr>
<th>TMM</th>
<th>ϕ1°</th>
<th>ϕ1′</th>
<th>ϕ2</th>
<th>ϕ2′</th>
<th>d1, Å</th>
<th>d2, Å</th>
<th>φ1</th>
<th>φ2</th>
<th>φ3</th>
<th>φ1 + φ2 + φ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structure 1]</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.635</td>
<td>1.445</td>
<td>146.8</td>
<td>136.2</td>
<td>109.0</td>
</tr>
<tr>
<td>![Structure 2]</td>
<td>2.6</td>
<td>1.7</td>
<td>5.2</td>
<td>5.1</td>
<td>4.6</td>
<td>5.7</td>
<td>1.926</td>
<td>1.432</td>
<td>131.6</td>
<td>130.5</td>
</tr>
<tr>
<td>![Structure 3]</td>
<td>23.4</td>
<td>22.1</td>
<td>21.1</td>
<td>20.4</td>
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<td>2.161</td>
<td>1.430</td>
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<td>123.3</td>
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<tr>
<td>![Structure 4]</td>
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<td>1.440</td>
<td>121.3</td>
<td>122.6</td>
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<tr>
<td>![Structure 5]</td>
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<td>72.6</td>
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<td>1.464</td>
<td>128.4</td>
<td>117.8</td>
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</table>

*All values of ϕ (degrees) are reported as deviations from 0° or 180°, whichever was closer. * The MM2-minimized structures of the analogous fulvenes were modified to provide the starting structures for the minimization, except where indicated. MOPAC as implemented in InsightII version 2.1.2 (BioSym) was used with the following parameters: triplet state spin-unrestricted, BFGS minimization type, line minimizer off. PRECISE keyword activated, 0.01 kcal/mol convergence criterion. Frequency calculations showed that all structures are true minima; all elements of the diagonalized force constant matrix were positive.

Supplementary Material Available: Full description of X-ray structures of 8 and 9 including atomic coordinates and interatomic distances and angles (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Dedicated to the memory of Gerhard Clow, who taught and inspired us all.


Acknowledgment. We thank the National Science Foundation for support of this work. S.K.S. thanks the NSF for a predoctoral fellowship.

(12) We have prepared several other derivatives of 4 in which the benzene ring is replaced by a pyridine, a phenol, or a phenoxide. In all cases, behavior similar to that seen for 4 is displayed. Silverman, S. K., unpublished results.

(13) TMMs of the present type are completely stable to the photolysis conditions, so photodestruction of the molecule is not a viable explanation.


(17) Fulvene (Xr(nm) in CH2Cl2): 11f (267), 10f (300), 19f (324), 18f (345), 17f (341, with extensive fine structure).

(18) All Δms = 2 hyperfine couplings are well simulated by a binomial distribution of Gaussian peaks. This is a valid procedure for systems with small D values. See, for example: Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. J. Am. Chem. Soc. 1988, 110, 1356-1366.


(22) The temperatures over which the changes in Figure 10 occur seem consistent with other examples of hindered methyl rotation.


(25) The diphenyl derivative of 3 shows considerable variation in the zfs E parameter.


