deprotected starting material **23** (0.11 g, 43%) and a mixture of **24t** and **24c** (0.054 g, 21%).

43: TLC (5% EtOAc/hexane) R_f 0.34; IR (neat) 3020, 1610, 1250, 1210, 1075, 1030, 880, 845 cm^{-1}; ^{1}H NMR (360 MHz) δ 0.17 (s, 9 H), 0.92 (s, 9 H), 1.68 (d, J = 1.1 Hz, 3 H), 1.81 (d, J = 1.4 Hz, 3 H), 2.82 (dt, J = 15.3, 3.7 Hz, 1 H), 5.62 (d, J = 10.1 Hz, 1 H), 5.68 (br s, 1 H), 6.06 (dd, J = 10.3, 2.3 Hz, 1 H); LRMS m/z (relative intensity) 292 (5). Silyl trienol ether **42** was approximately 75% pure as determined by ^{1}H and ^{13}C NMR and GC analyses. Contaminants included a stereoisomer [13% by GC; LRMS m/z (relative intensity) 292 (7)] and two unidentified components.

Note Added in Proof

Fehr reported that (trimethylsilyl)oxy derivatives of *all-cis*-hexatrienes undergo cyclization under pyrolysis conditions (0.8 mL/min, 365 °C) but that the trans isomers were returned unchanged.[49] These results are consistent with our observation that the thermal cyclization of SOH **12** proceeds very slowly at 110 °C.

Acknowledgment. We gratefully acknowledge support for this project by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Office of the Vice President for Research at the University of Iowa. Palladium was generously loaned through the Johnson Matthey Precious Metal Loan Program. (*Z*)-Prop-1-en-1-yltributylstannane was a gift from Bristol-Myers Co. for which we thank Dr. Vittorio Farina and Dr. Greg Roth. Mass spectra were obtained in the University of Iowa High Resolution Mass Spectrometry Facility. FAB-MS analyses were performed by Dr. Larry M. Mallis. NMR spectra were obtained in the University of Iowa High Field NMR Facility. We thank Professor Samuel Danishefsky (Yale University) for informing us of ref 8, Professor Derek H. R. Barton (Texas A & M University) for informing us of ref 6, and Dr. Vittorio Farina of Bristol-Myers Co. for providing preprints of his work with tri-2-furylphosphine.

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Synthesis, Structure, and Properties of a 2-(Trimethylsilyl)cyclobutenocyclooctatetraene

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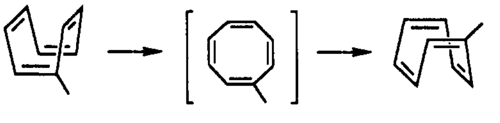
Abstract: The first example of the cyclobutenocyclooctatetraene structural class (**2**) to possess stability at room temperature has been prepared by a route involving ring contraction via a Wolff rearrangement. Derivatives have been characterized by various spectroscopic techniques, X-ray crystallography, and cyclic voltammetry. All of these properties are in concert with a structure possessing a high-lying HOMO, low-lying LUMO and a carbon skeleton closer to planarity than any bicyclic cyclooctatetraene yet prepared.

Introduction

Cyclooctatetraene has drawn attention as the vinylog of benzene since it was first prepared by Willstatter in 1911.[2] This interest was further intensified by Huckel's 1937 proposal[3] that a 4n π-electron system, such as is superficially present in cyclooctatetraene, should possess an unfavorable electronic delocalization. That cyclooctatetraene itself could exist as a stable molecule yet not violate this canon was made explicable by its structural characterization as a nonplanar "tub" form[4] possessing alternating double and single bonds.[5]

Two approaches have been taken to reveal possible 4n cyclic conjugation in cyclooctatetraenes, both involving synthesis of analogues. The first is based on the known isomerizations of cyclooctatetraenes, for which two modes are available because of their nonplanarity and alternating bonds. Ring inversion (eq 1) relates to conformational mobility and enantiomerization and can proceed through a planar D_{4h} transition state with alternating bonds. Extensive measurements on the inversion barriers of cyclooctatetraenes have been made.[6] Bond shifting (eq 2) relates to *constitutional isomerism* and for the most part has a higher activation energy than inversion.[6,7] While it seems intrinsic that the transition state for bond shifting is fully conjugated, recent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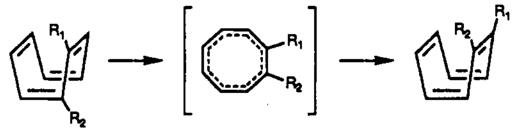

(2)

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work by Paquette[8] has implicated a pseudorotation mechanism that avoids the antiaromatic nature of a fully conjugated transition state. Thus, a long-standing approach to address the antiaromaticity of a 4n system, that is measuring the energy difference (2–4 kcal/mol) between the alternating and fully conjugated transition states involved in ring inversion and bond shifting and assuming that it is reflective of the antiaromatic nature of the latter, has been invalidated.

A different tactic, i.e., the introduction of conformational constraints into the cyclooctatetraene framework, has provided planar versions suitable for physical studies. Given the small contribution of resonance energy to the overall barrier for planarization of cyclooctatetraene,[9] the more important bond angle distortions and van der Waals interactions that are intuitively understood by organic chemists have been manipulated according to well-established principles. While a number of planar cyclooctatetraenes embedded within polycyclic aromatics have been prepared,[10] most are unsuitable for X-ray analysis and/or lack protons on their 4n periphery so as to judge their antiaromatic nature by NMR. The moderating influence of benzofusion on the intrinsic properties of the planar 4n system also makes them suspect.

Unconjugated planar cyclooctatetraenes are known, though. One such compound is perfluorotetracyclobutenocyclooctatetraene (**1**).[11] Its alternating bonds (though the difference between the double (1.35 Å) and single (1.43 Å) bonds is less than in related structures) are localized as shown. The ability of this compound to attain the planar conformation can be explained through two effects. The double bond localization avoids antiaromaticity, and the small internal bond angle of the cyclobutane ring permits the accommodation of the 135° internal angle of an octagon into the framework of **1** without strain. The presence of the perfluorocyclobuteno groups in **1** is only a consequence of the cascade-like synthetic route and in fact has several disadvantages for those interested in the properties of an antiaromatic cyclooctatetraene. One cost of this tactic is bond alternation. Once again, there are no protons to signal a paramagnetic ring current, and the "perfluoro effect"[13] may mask the antiaromatic properties of the "naked" cyclooctatetraene by considerably lowering the overall orbital energies. Theoretical study suggests that the fusion of only two cyclobutane rings to a cyclooctatetraene should be sufficient to relax the tub to a planar form.[12] It has also been suggested[14] that while a cyclooctatetraene otherwise identical with **1** but bearing no fluorines should have a similar planar structure,[12] its calculated first ionization potential of 6.9 eV would render it sensitive to air oxidation. Another known cyclobutene-annulated cyclooctatetraene, the parent system **2**,[15] readily polymerizes when concentrated. However, recent efforts by Houk and Diederich have shown by calculation (AM1) and experiment that cyclobutene annulation stabilizes macrocyclic annulenes.[16] Thus, directed syntheses of cyclobutene-annulated cyclooctatetraenes possessing other stabilizing features would advance us toward the goal of planar cyclooctatetraenes, compounds desirable for physical study.

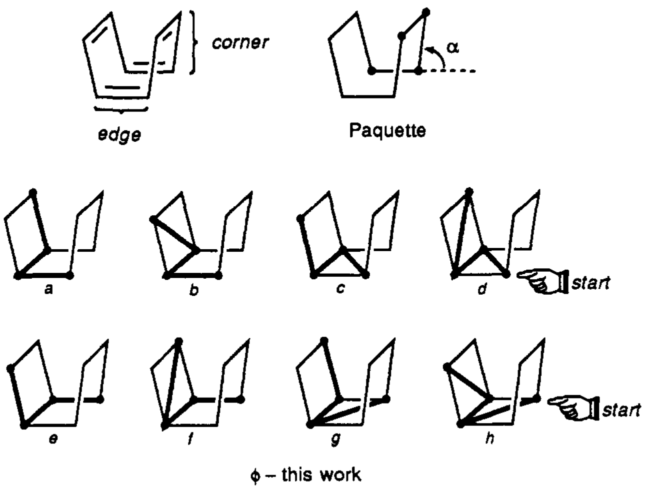
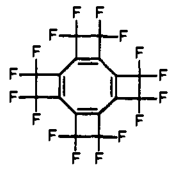


Figure 1. Cyclooctatetraene geometries.



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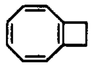

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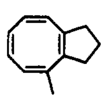

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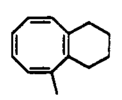

4

The synthesis of substituted cyclooctatetraene analogues has been important to the development of the large literature on antiaromaticity in [8]annulenes as well as other areas such as sandwich complexes of the transuranium elements.[17] None of the extant methods is readily modified to permit the synthesis of cyclooctatetraenes annulated with multiple small rings. Such compounds were postulated by Ermer[18] to possess the conformational restriction necessary to produce a nonalternating, fully planar cyclooctatetraene. We reported in 1987 a photochemical acetylene cycloaddition method[19] that yields (trimethylsilyl)cyclooctatetraenes annulated to cyclopentanes. This work was based on Morrison's brief report of an analogous, low yielding reaction with an alkyl acetylene.[20] Morrison's procedure was subsequently used by Paquette to prepare quantities of the five-ring annulated derivative **3** for study.[21] It is notable that while the cyclohexeno-annulated derivative **4** and its bond shift isomer can both be obtained (though by a different route), **3** is a single isomer. Inspection of molecular models provides a ready explanation for this phenomenon. Since the bonds projecting from the "edge" of the cyclooctatetraene tub (Figure 1) are nearly coplanar for most cyclooctatetraenes, the smallest of rings can be accommodated across them without adding torsional strain to the system. However, the bonds at the "corners" (vicinal, but from different π bonds) are skew, and their degree of skew is dependent on the flatness or "tub-ness" of the cyclooctatetraene. This skew angle ranges from 66.6° in octamethylcyclooctatetraene to 0° in a completely planar system. As will be exposed below, this dihedral angle does not best describe the nonplanarity of a cyclooctatetraene. It is apparent, however, that the larger the angle, the more difficult it will be for a small ring to be fused across these two bonds. The consequence of cyclopentannulation (or even a

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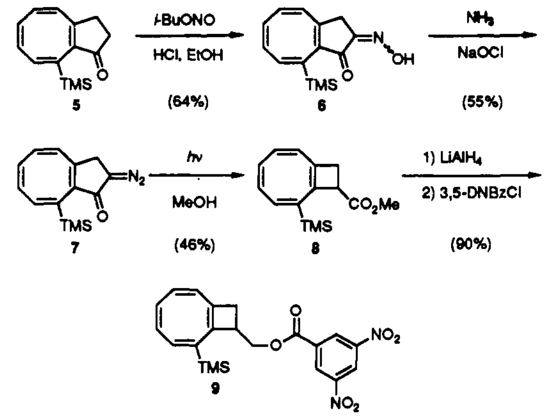
Scheme I



smaller fusion) is that only the isomer having the aliphatic ring fused at the edge is observed. Empirical force field (EFF) calculations performed in our laboratory suggest that K_{eq} for equilibration of 3 with its bond shift isomer would be $<10^{-7}$. Conversely, if a small ring is *required* to be annulated across a corner through a directed synthesis, it will have the effect of flattening the cyclooctatetraene ring. Indeed, this is the basis of the structural proposals of Ermer.[18]

Results

Synthesis. The route adopted for the preparation of the cyclobutene-annulated cyclooctatetraene (Scheme I) was based on a similar sequence used in an early synthesis of benzocyclobutene from indanone.[22] The indanone homolog **5** is available by oxidation of the corresponding carbinol obtained from previous work.[19] Conversion to the oxime ketone **6** and thence to the diazoketone **7** proceeds without incident. Diazotransfer to **5** via the corresponding formyl ketone is unsuccessful. Wolff rearrangement of **7** affords the ester **8**, which was used for the physical studies in order to avoid problems with absorption and electrochemical reduction of the benzoate in **9**. Crystalline derivative **9** was prepared for X-ray structure determination.

Structure. Crystallographic data for **9** are collected in Table I, and a stereoplot of the structure is presented in Figure 2. The cyclobutenocyclooctatetraene core is bisected at the C_4–C_5, C_1–C_8, and C_9–C_{10} bonds by an approximate mirror plane of symmetry. Structural parameters for this core are recorded in Figure 3. The bond lengths are typical based on known cyclooctatetraene structures and clearly demonstrate the alternating nature of the C–C distances as well as the double bond localization in the ring fusion. Although the mean of the cyclooctatetraene bond angles at 127.8° is normal for these systems, enlargement of angles at atoms shared with the planar cyclobutene ring to 131.9° and 132.7°, i.e., toward the ideal octagonal value of 135°, is evident, as is the associated flattening as reflected in the smaller torsional angles around the C_1–C_2 and C_7–C_8 single bonds versus those around the C_3–C_4 and C_5–C_6 bonds. Departure from exact C_s symmetry-related distances and angles in the C_1–C_4/C_5–C_8 regions of the molecule may be ascribed to the steric influence of the trimethylsilyl substituent. Its bulk prevents adoption of the shorter bond lengths and smaller bond and torsion angles found in the C_5–C_8 region, where they may be more representative of the influence of cyclobutene fusion.

Table 1. Crystallographic Data[a]

molecular formula	$C_{21}H_{22}N_2O_6Si$
formula weight	426.51
crystal system	monoclinic
space group	$P2_1/c(C_{2h}^5)$—no. 14
a (Å)	18.234 (2)
b (Å)	16.725 (2)
c (Å)	7.234 (1)
β (deg)	96.63 (1)
no. of orientation reflcns; θ (deg) range	25; 42–47
V (Å^3)	2191.4 (8)
Z	4
D_{calcd} (g cm^{-3})	1.293
μ (Cu Kα radiation, λ = 1.5418 Å) (cm^{-1})	12.6
temp (°C)	23
crystal dimensions (mm)	0.06 × 0.28 × 0.48
T_{max}:T_{min}	1.00:0.85
scan type	ω–2θ
scan width (deg)	1.00 + 0.14 tan θ
θ_{max} (deg)	75
intensity control reflcns; variation; repeat time (h)	112, 21$\bar{2}$, 13$\bar{1}$, 121; <1%; 2
total no. of reflcns ($+h$,$+k$,$\pm l$) recorded	4860
no. of nonequiv reflcns recorded	4489
R_{merge} (on I)	0.017
no. of reflcns retained [$I > 3.0\sigma(I)$]	2587
no. of parameters refined	360
extinction correction	7.0 (9) × 10^{-7}
R (R_w)[b]	0.040 (0.051)
goodness-of-fit[b]	1.37
max shift:esd in final least-squares cycle	0.02
final $\Delta\rho$(e/Å^3) max; min.	0.18; −0.18

[a] An Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, incident-beam graphite monochromator) was used for all measurements. Intensity data were corrected for the usual Lorentz and polarization effects; an empirical absorption correction was also applied. The crystal structure was solved by direct methods (MULTAN11/82). Initial non-hydrogen atom coordinates were derived from an *E*-map. Hydrogen atoms were all located in a difference Fourier synthesis evaluated following several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic temperature factor parameters, and their positional and isotropic thermal parameters were included as variables during the subsequent least-squares iterations. An extinction correction was also refined during the later least-squares cycles. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package. For the structure factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from International *Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $\sum w\Delta^2[w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)]$ was minimized; goodness-of-fit = $[\sum w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Quantitating the degree of flattening of the cyclooctatetraene ring by cyclobutene annulation is *key*. In his work on annulated cyclooctatetraenes,[21] Paquette proposed a term "external dihedral angle", or α (Figure 1), that is intended to reflect the degree of nonplanarity of a cyclooctatetraene. He reported α for EFF structures of several cyclooctatetraenes that he prepared as well as more than ten whose X-ray structures are in the Cambridge database. Because of poor definition of the method of determining α and its questionable significance,[23] we have developed our own measure, ϕ for flap angle, of the nonplanarity of a cyclooctatetraene. It is the absolute value of the acute dihedral angle between two planes defined by the "bottom" and "sides" of the tub. A fully planar cyclooctatetraene would show ϕ = 0°. A single value of ϕ is easily determined by using the dihedral angle feature found in most molecular modeling systems simply by selecting four atoms in succession and subtracting the value obtained from 180°. For a given flap (bottom-side pair), there are eight sequences of atoms that define a dihedral (Figure 1), but only four (a, b, e, and f) are independent measurements. If the cyclo-

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(22) Horner, L.; Kirmse, W.; Muth, K. *Chem. Ber.* **1958**, *91*, 430.

(23) The definition given in ref 21 is as follows: α = the angle between a plane described by three contiguous cyclooctatetraene atoms and a line defined by the projection of the bond between one of the terminal atoms of the three and its remaining endocyclic bonding partner (Figure 1). Actually, the α values reported by Paquette are the dihedral angles between a least-squares plane formed from the bottom of the tub and a second plane defined by the three indicated side atoms in Figure 1 (Galucci, J., personal communication). With this clarification it is still difficult to draw structural insight into a particular cyclooctatetraene from even a few α values, particularly those calculated from crystal structures. Despite high molecular symmetry, crystal packing forces can exert a significant perturbation on local structure and cause a wide variation in α. All of the α values for a structure would therefore be required to draw meaningful conclusions, and these were not provided in Paquette's work.

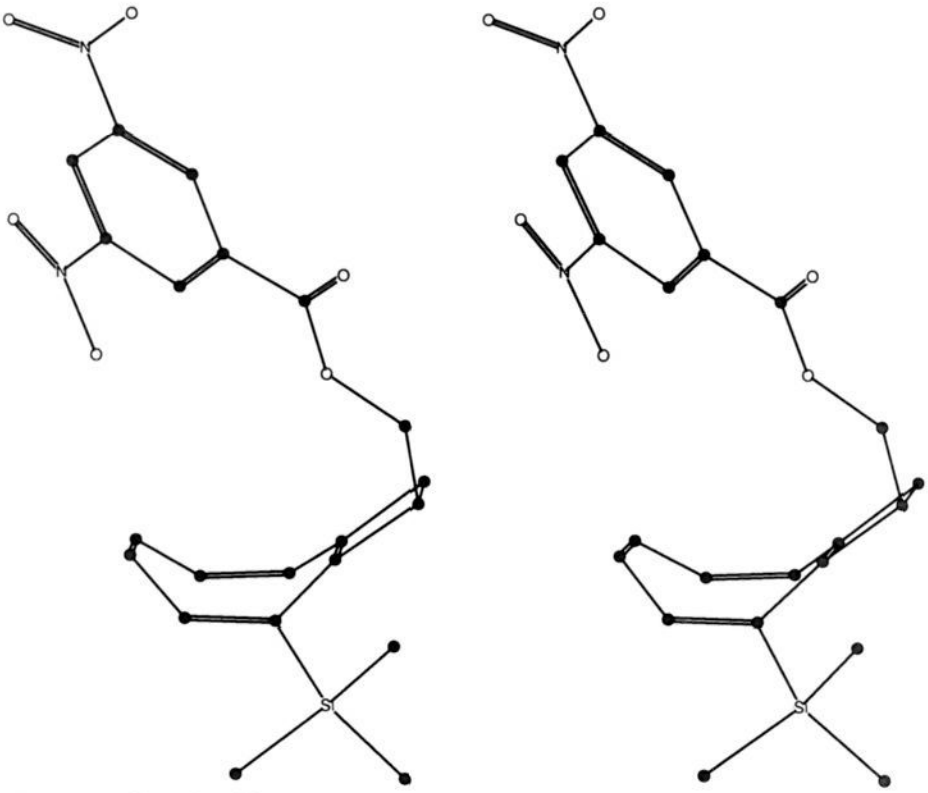


Figure 2. X-ray crystal structure of **9** as plotted by CHEM 3D.

Table II. Variation of ϕ for **9**

atom sequence	$\phi_{\text{X-ray}}$	ϕ_{MMX}
6, 7, 2, 1	39.1	38.0
3, 2, 7, 8	40.8	38.2
2, 3, 6, 5	39.4	37.1
7, 6, 3, 4	43.5	38.7
4, 5, 8, 7	33.8	32.1
1, 8, 5, 6	39.0	34.2
5, 4, 1, 2	37.9	34.2
8, 1, 4, 3	38.3	35.1

Table III. Physical and Structural Data for Cyclooctatetraenes[a]

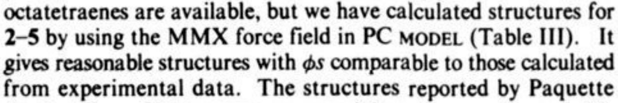
compd	J_1	J_2	$\phi_{\text{X-ray}}$ (deg)	ϕ_{MMX} (deg)
2				30
3	2.6	2.8		43
4	3.6	3.7		48
5	3.4	3.5		44
8	3.6	3.9		35
9	4.3	3.9	39	36

[a] J_1 and J_2 are the 3,4 and 5,6 coupling constants, and ϕ_{MMX} is the value of ϕ derived from an empirical force field structure.

octatetraene ring is C_s symmetric, angles a and e (and b and f) are related by a mirror plane and are equivalent. In reality, even molecules with nominal D_{2d} symmetry show significant differences between measurements of a and e. Under ideal D_{2d} symmetry, all ϕs must be equal. For cyclooctatetraenes of lower symmetry, their difference provides information about structure-induced distortions. While dihedral angles b and f are not exactly equivalent to a and e, the mean of measurements a and e is the same as the mean of b and f. For this reason it is sufficient to define ϕ for a given flap as the mean of the two angles a and e. Since there are two sides for each bottom, there are four ϕs per tub. However, there are two tubs per cyclooctatetraene, each bottom being defined by one 1,5-diene pair. This proliferation of ϕs in some ways makes the structure harder to visualize, but it does provide information about distortions as mentioned above. To simplify tabulation of individual ϕs, we have written a simple computer program (available upon request) that calculates the ϕs given the Cartesian coordinates. Its output for compound **9** is summarized in Table II. Eight individual ϕs are given, with the corresponding atom sequence listed. The mean value of ϕ for **9**, based on X-ray data, is 39°. The flattening effect of the cyclobutene fusion is evident from the ϕs of 38.1 and 36.4°. The flattening occurs not in the flap onto which the ring is fused but in the side flaps.

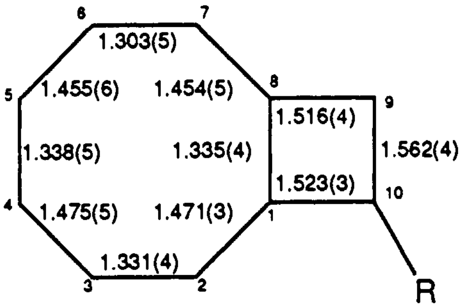
The skew angle is an obvious structural parameter to use as a measure of cyclooctatetraene nonplanarity because it relates to a physical property, i.e., a vicinal coupling constant. The relationship between the skew angle of bonds to cyclooctatetraene substituents and the flap angle is not simple. Figure 4 shows the dependence of ϕ on the skew angle for cyclooctatetraene.

Table IV. ϕ for Known Cyclooctatetraenes

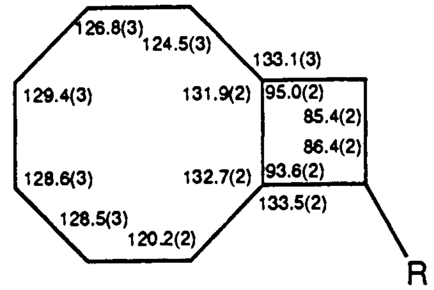


It is desirable to compare the ϕ values for **9** to known compounds. No other crystal structures of singly annulated cyclooctatetraenes are available, but we have calculated structures for **2–5** by using the MMX force field in PC MODEL (Table III). It gives reasonable structures with ϕs comparable to those calculated from experimental data. The structures reported by Paquette (derived from Still's MODEL program) have large variances with experiment. For example, MMX produces a minimized structure for cyclooctatetraene with ϕ = 43°, while Paquette reports α = 48.2°, and the electron diffraction structure gives ϕ = 41°. Mean flap angles ϕ for known cyclooctatetraenes based on crystal structures are summarized in Table IV.

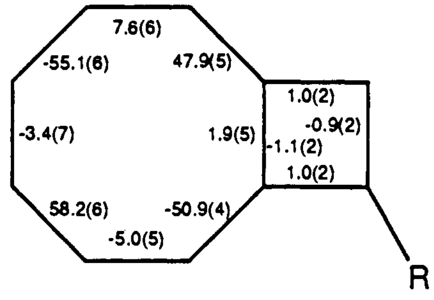
Two alternative means to induce planarity in cyclooctatetraenes can be drawn from the literature. Since the skew angle between



bond lengths



bond angles



torsion angles

Figure 3. Structural parameters for cyclooctatetraene **9**. Estimated standard deviations are given in parentheses.

vicinal hydrogens on adjacent double bonds is 0° in a planar cyclooctatetraene, requiring a 0° dihedral angle by a small ring fusion should produce at least local planarity analogous to butadiene. This concept is the basis of the structures proposed by Ermer. Another requirement is that bond shifting may not produce a more stable structure, and ideally it would produce the *same* structure. Alternatively, a small ring fusion on one of the double bonds concomitantly opens the bond angles external to the small ring and internal to the cyclooctatetraene. This was one explanation for the planar structure of **1**. In order to address which component of small ring fusions is most important in flattening cyclooctatetraenes, calculations were conducted on cyclooctatetraene itself under two different constraints: one skew angle at 0°, or two vicinal internal C–C–C bond angles at 135°. Only the former leads to a completely planar structure. The ϕs for the latter (C_s symmetric through the single bonds) are 35.7° and 30.3°. Thus, only the strategy of constraining dihedral angles is by itself sufficient to planarize cyclooctatetraenes. It should be possible, though, to achieve this goal by combining two constrained internal angles, as indicated by previous theoretical study.[12]

Electrochemistry. In order to evaluate the influence of flattening on the electronic structure of cyclooctatetraene, the reduction potential of **8** was measured by cyclic voltammetry. Previous measurements of cyclooctatetraene reduction potentials have been used to evaluate the influence of planarity in the ground-state and steric interactions of vicinal substituents in the planar aromatic dianion. The former should make the cyclooctatetraene easier to reduce, while the latter should hinder reduction. In making meaningful comparisons between cyclooctatetraenes, the effects of solvation, anion stabilization, aromaticity, and other factors must be virtually constant.

The CV of **8** is shown in Figure 4. Reduction occurs at −0.985 V vs SCE, with the symmetric reverse sweep showing that the reduction is reversible. While we do not have coulometry data to prove that this is a two-electron reduction, no other waves are observed to at least 1 V more negative potential. It is therefore likely that both electrons are accepted at this potential, an observation that is precedented in other cyclooctatetraenes.[24] This is the least negative potential for a cyclooctatetraene reduction that has yet been reported. It is suggested that the trimethylsilyl group contributes little to this facile reduction, since the known potentials for cyclooctatetraene (−1.606 and −1.921 V) and (trimethylsilyl)cyclooctatetraene (−1.64 and −1.84 V) are very similar.[25] Other alkylcyclooctatetraenes whose reduction potentials have been measured are the 1,2,3-trimethyl derivative (−2.2 V), the 1,2,3,4-tetramethyl derivative (−2.54 V), and the 1,5-dimethyl derivative (−1.94 and −2.28 V).[26] The obvious expla-

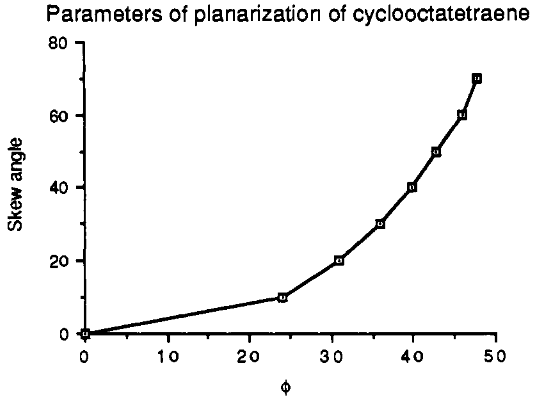


Figure 4. Planarization parameters for cyclooctatetraene.

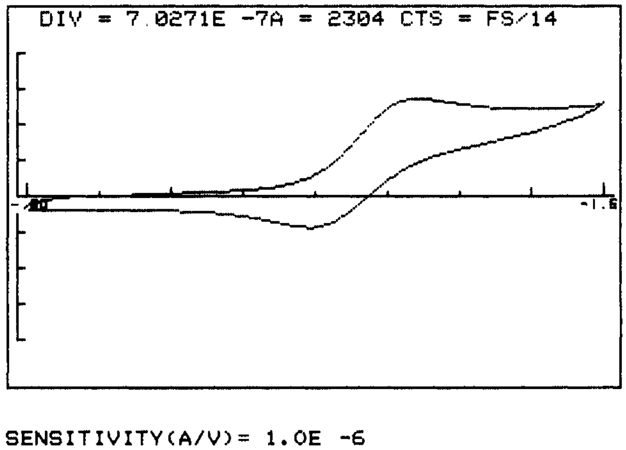


Figure 5. Cyclic voltammogram of **8** obtained in HMPA/TBAP, recorded at 100 mV/s. The reference electrode was Ag/Ag$^+$. In the anodic sweep, the peak potential is −1191 mV, and the current is 0.88 mA. In the cathodic sweep, the peak potential is −1345 mV, and the current is 1.54 mA. The potential quoted in the text was corrected to SCE by adding 0.36 V.

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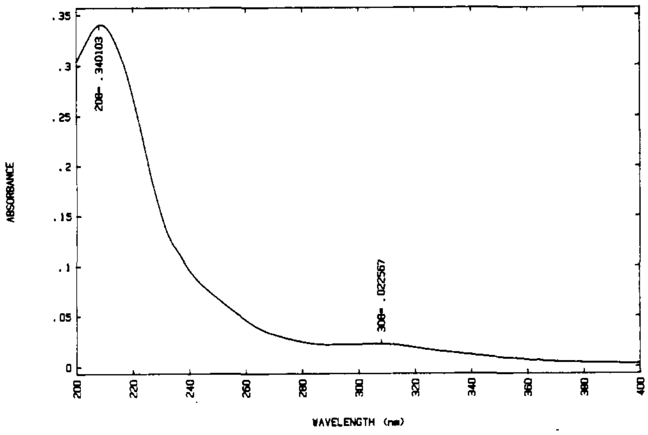


Figure 6. Ultraviolet spectrum of **8** measured at 24 mM in hexane.

nation for the reduction potential of **8** is the flattening of the ring that distorts the ground state toward that of product and concomitantly lowers the LUMO.

Spectral Data. Most simple cyclooctatetraenes show end absorption and fairly large shoulders at ca. 280 nm.[27] The UV-visible spectrum of **8**, in Figure 5, shows the long wavelength band red-shifted to 308 nm. Its extinction coefficient of ~3500 far exceeds that for 1,2-dimethylcyclooctatetraene (λ_{max} = 270 nm, ϵ 440) and is greater than the highest previously reported for a nonconjugated cyclooctatetraene by more than an order of magnitude. The red-shift of this band resembles that of 1,4-dicyanocyclooctatetraene (λ_{max} = 217 nm, ϵ 26 000; λ_{max} = 307 nm, ϵ 720).[28] Interestingly, in contrast to **8**, Sondheimer reports that **2** has no λ_{max} above 220 nm. It is unclear whether this might indicate that **2** has significant absorption (a "tail") in this long wavelength region but no local maximum. These observations are in concert with previous results[29] that the 280-nm band in the absorption spectrum of cyclooctatetraene is the HOMO–LUMO transition ($5a_1(\pi) \rightarrow 3a_2(\pi^*)$) to the first singlet state. Planarization of the ring in **8** will raise the HOMO, causing intensification and red-shift in the band. In the (trimethylsilyl)cyclooctatetraenes previously prepared,[19] such long wavelength bands are absent; it can thus be inferred that these compounds are reluctant to planarize.

The NMR data of **8** and **9** resemble those of other compounds in the (trimethylsilyl)cyclooctatetraene series. The coupling constants for **9** shown in Table II of 3.9 and 4.3 Hz correspond to the torsion angles in Figure 3 of 58 and 55°. These compare to predictions based on the modified Karplus equation of 4.7 and 4.3 Hz.

Quenching Properties. Cyclooctatetraene is widely known as an excited-state quencher and is utilized to quench triplets in laser dyes.[30] Data are absent, however, relating cyclooctatetraene structure to quenching properties. This question was addressed with **8** in two experimental systems: the quenching of biacetyl fluorescence and of an intramolecular aryl ketone triplet cycloaddition. Stern–Volmer plots for the first system, spectroscopically determined by the method of Turro and co-workers[30] for both **8** and cyclooctatetraene itself, are shown in Figure 6. A k_q of 5.4 × 10^7 M^{-1} s^{-1} had previously been reported for quenching of camphorquinone fluorescence by cyclooctatetraene.[31] For biacetyl quenching, the k_q is 1.09 × 10^9 M^{-1} s^{-1} for cyclooctatetraene, while it is 1.2 × 10^{10} M^{-1} s^{-1} for **8**. The quenching of the cycloaddition of **10** to give **11** by dimethylhexadiene has $k_q\cdot\tau$ of 110 M^{-1}.[32] For cyclooctatetraene, $k_q\cdot\tau$ is 40 M^{-1}, whereas **8** shows $k_q\cdot\tau$ of 70 M^{-1} (Figure 7). Thus, compound **8** is a 2- to 10-fold better quencher than cyclooctatetraene itself.

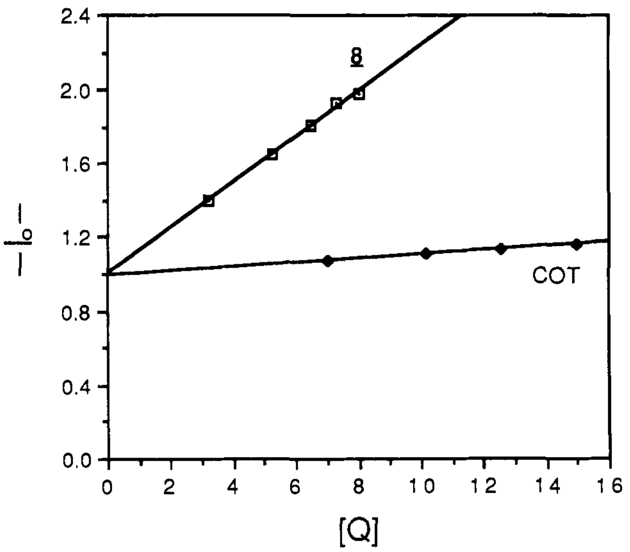


Figure 7. Stern–Volmer plot of the quenching of biacetyl fluorescence at 2.6 × 10^{-2} M in benzene by cyclooctatetraene and **8**, with concentration of quencher in mM. The slope $k_q\cdot\tau$ = 0.0109 mM^{-1} for the former and 0.1229 mM^{-1} for the latter.

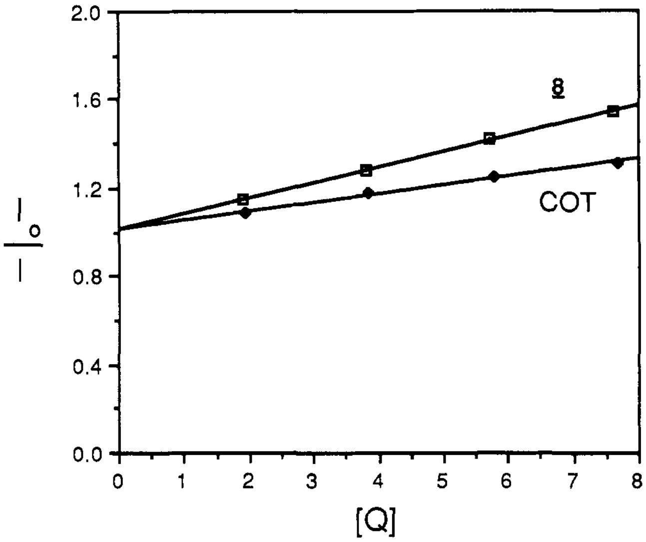
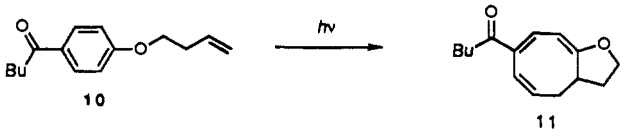


Figure 8. Stern–Volmer plot (product quantum yield) of the quenching of the cycloaddition of **10** (0.01 M in degassed acetonitrile) by cyclooctatetraene and **8**, with concentration of quencher in mM. The slope $k_q\cdot\tau$ = 0.0396 mM^{-1} for the former and 0.0696 mM^{-1} for the latter.



Twisting the π system of a quencher reduces its effectiveness even in exothermic energy transfer. For example, 1,3-cyclooctadiene quenches acetophenone triplet with k_q of 2 × 10^9 M^{-1} s^{-1} compared to the k_q of 5 × 10^9 M^{-1} s^{-1} for dimethylhexadiene.[33] Temperature dependence studies further suggest that this lower efficiency is due not to the higher triplet energy of the twisted

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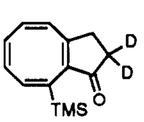
π-system but to its reduced ability to form an exciplex. We can interpret the behavior of **8** based on this analogy. Cyclooctatetraene ($E_T \sim 70$ kcal/mol) is a poorer quencher than **8** because its ability to quench via exciplexes is diminished by its less planar π-system.[34] The closer that analogues of cyclooctatetraene approach planarity due to conformational restraints, the better quenchers they should be. The determination of the triplet energy of **8** is needed to support this contention. Theoretical consideration of the cyclooctatetraene triplet has suggested it should be aromatic,[35] but the level of theory used has not resolved whether it is planar (like the biphenyl triplet).[36] This is another area for future research. On the other hand, quenching of triplet ketones by alkenes has been shown to occur via charge transfer.[37] The higher HOMO already demonstrated for **8** would make it superior in this capacity.

Dynamics. Study of the rate of enantiomerization of cyclooctatetraene derivatives has lost its value in addressing issues of antiaromaticity for reasons discussed earlier. It was of interest to evaluate how cyclobutane annulation and the resultant ring flattening affect the inversion barrier to compare with the large body of previously acquired data on such phenomena. Unfortunately, neither **8** nor **9** show temperature dependence in their NMR spectra. Because both compounds possess two elements of chirality, they potentially exist as two *diastereomers* interconvertible by cyclooctatetraene inversion. Spectral evidence suggests that only one conformer is present in both **8** and **9**, and it is reasonable that the conformation seen in the crystal (Figure 2) is also found in solution. This conformer has the virtue that the maximal distance between the substituent on the cyclobutane ring and the bulky trimethylsilyl group is maintained. Thus, dynamic NMR effects for **8** and **9** are absent not because of the kinetics of the inversion process but because of the thermodynamics. There is nothing intrinsic to the presence of the trimethylsilyl group that raises the inversion barrier, since **5** has one of the lowest ever reported for a 1,2,3-trialkylcyclooctatetraene. Its value was determined with the dideuterated derivative **12**, which



12

has a T_c for the diastereotopic allylic methylene protons of 60 °C in acetone-d_6. Deuteration permits the observation of these protons as a simple AB pattern, and, through a standard treatment,[38] a barrier of 16.7 kcal/mol can be calculated. This compares to the 24.4 kcal/mol barrier in 1,2,3-trimethylcyclooctatetraene.

Conclusion

This study represents the first step toward the synthesis of cyclooctatetraenes that are constrained to planar conformations by small ring fusions. Such compounds will be useful in answering questions about the cost of 4n conjugation and possible antiaromaticity in small annulenes. The route is simple and should be applicable to more highly substituted systems. The fact that compounds **8** and **9** are stable at room temperature, whereas **2** is not, suggests that the trimethylsilyl group may serve to stabilize even more highly planarized cyclooctatetraenes. The characteristics of the compounds we have prepared are suggestive that this class will possess interesting properties connected with their planarity.

Experimental Section

2-(Trimethylsilyl)bicyclo[6.3.0]undeca-2,4,6,8(1)-tetraen-11-one (5). In a 100-mL flask fitted with a guard tube was suspended 1.2 g (3.0 mmol) of pyridinium dichromate in 50 mL of anhydrous dichloromethane. To this suspension was added 600 mg (2.3 mmol) of the known alcohol,[19] and the reaction mixture was stirred at room temperature for 12 h. The contents were diluted with 100 mL of anhydrous ether, the supernatant was poured off, and the remaining solid was washed with 50 mL of anhydrous ether. The combined organic layer was filtered through a short pad of Florisil and concentrated to give a crude product which was recrystallized from petroleum ether–dichloromethane to afford ketone (420 mg) in 70% yield: mp 123.5 °C; IR (Nujol) 1685, 1640, 1620, 838 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.18 (1 H, d, $J = 3.5$), 6.04 (1 H, d, $J = 11.7$), 5.96 (1 H, dd, $J = 11.1, 3.4$), 5.91 (1 H, dd, $J = 11.7, 3.4$), 5.64 (1 H, dd, $J = 11.7, 3.4$), 2.48 (4 H, m), 0.08 (9 H, s); HRMS (M + 1), calcd for $C_{14}H_{20}OSi$ 231.1205, found 231.1198. Anal. Calcd for $C_{14}H_{19}OSi$: C, 73.00; H, 7.88. Found: C, 73.10; H, 7.94.

10-Oximido-2-(trimethylsilyl)bicyclo[6.3.0]undeca-2,4,6,8(1)-tetraen-11-one (6). In a 50-mL flask was placed 300 mg (1.3 mmol) of ketone **5**, 5 mL of ethanol, and 0.1 mL of water. To this mixture was added 150 mg (1.5 mmol) of isobutyl nitrite followed by 0.1 mL of concentrated hydrochloric acid, and the reaction mixture was stirred at room temperature for 6 h. Ethanol was removed at reduced pressure, and the residue was extracted with ether (3 × 50 mL). The combined ethereal extract was washed with saturated $NaHCO_3$ and brine and dried over anhydrous Na_2SO_4. The crude product obtained after removal of the solvent was flash chromatographed on a 5-g silica gel column, eluting with 5% ethyl acetate–petroleum ether, and finally recrystallized from petroleum ether to afford pure crystalline oximido ketone (200 mg) in 64.5% yield as a 1:2 (inseparable) mixture of stereoisomers: IR (Nujol) 3343, 1708, 1618, 1247 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.25–5.68 (10 H, series of d), 3.26 ($^1/_2$ H, d, $J = 24$), 3.24 ($^1/_2$ H, d, $J = 24$), 3.03 ($^1/_2$ H, d, $J = 24$), 2.93 ($^1/_2$ H, d, $J = 24$), 0.12 ($^9/_2$ H, s), 0.11 ($^9/_2$ H, s); HRMS (M + 1); calcd for $C_{14}H_{18}NO_2Si$ 260.1106, found 260.1103.

10-Diazo-2-(trimethylsilyl)bicyclo[6.3.0]undeca-2,4,6,8(1)-tetraen-11-one (7). In a 50-mL flask was placed oximido ketone **6** (200 mg, 0.8 mmol) and 5 mL of 2 N NaOH was added. To this suspension a mixture of NaOCl (3 mL) and concentrated ammonia solution (5 mL) was added and stirred for 1 h. The reaction mixture was extracted with ether (3 × 50 mL), and the combined ethereal extract was washed with water and brine and dried over Na_2SO_4. Crude product obtained after removal of the solvent was flash chromatographed over silica gel (3 g), eluting with 5% ethyl acetate–petroleum ether, and then recrystallized from petroleum ether–ethyl acetate to afford crystalline diazo ketone (110 mg) in 55% yield: mp 150 °C; IR (Nujol) 2076, 1645, 1248, 1077 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.22 (1 H, d, $J = 3.2$), 6.05 (1 H, dd, $J = 11.1, 3.7$), 5.96 (1 H, d, $J = 11.7$), 5.93 (1 H, dd, $J = 11.6, 3.6$), 5.66 (1 H, dd, $J = 11.7, 3.9$), 3.40 (1 H, d, $J = 19.5$), 3.45 (1 H, d, $J = 19.5$), 0.12 (9 H, s); HRMS (M + 1), calcd for $C_{14}H_{17}ON_2Si$ 257.1110, found 257.1107.

Methyl 2-(Trimethylsilyl)bicyclo[6.2.0]deca-2,4,6,8(1)-tetraene-10-carboxylate (8). Diazo ketone **7** (50 mg, 0.2 mmol) was dissolved in 50 mL of degassed dry methanol and irradiated for 3 h with a Hanovia 450-W medium pressure mercury lamp with a Pyrex filter. The solvent was evaporated at reduced pressure, and crude product was flash chromatographed over a silica gel column, eluting with 5% ethyl acetate–petroleum ether, to afford methyl ester (24 mg) in 46% yield: IR (thin film) 2956, 1732, 1250, 838 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.91 (1 H, d, $J = 3.9$), 5.76 (1 H, dd, $J = 11.0, 4.3$), 5.62 (1 H, dd, $J = 11.9, 3.4$), 5.54 (1 H, d, $J = 11.0$), 5.51 (1 H, dd, $J = 11.9, 4.1$), 3.71 (3 H, s), 3.50 (1 H, m), 2.64 (2 H, m), 0.08 (9 H, s); UV (hexane) 210 nm, ϵ 21 300; 308 nm, ϵ 3540. Satisfactory analytical data were not obtained.

2-(Trimethylsilyl)bicyclo[6.2.0]deca-2,4,6,8(1)-tetraen-10-methanol. In a 50-mL flask fitted with a dry nitrogen gas inlet was placed lithium aluminum hydride (10 mg, 0.3 mmol), and 5 mL of dry ether was added. To this suspension was added methyl ester (25 mg, 0.1 mmol) in 3 mL of dry ether at 0 °C. The reaction mixture was stirred at room temperature for 0.5 h and then placed in an ice bath. The reaction was quenched by slow addition of 0.5 mL of water and 1 mL of aqueous 10% sodium hydroxide. The ether layer was filtered, and the solid remaining was washed thoroughly with another 50 mL of ether. The combined ethereal layer was washed with brine and dried over anhydrous Na_2SO_4. The crude material obtained after removal of the solvent was filtered through a small silica gel column by using 10% ethyl acetate–petroleum ether to afford pure alcohol (20 mg) in 95% yield: IR (thin film) 3358, 2931, 1248, 837 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.91 (1 H, d, $J = 3.4$), 5.73 (1 H, dd, $J = 11.2, 4.0$), 5.62 (1 H, dd, $J = 11.7, 3.8$), 5.61 (1 H, d, $J = 11.0$), 5.54 (1 H, dd, $J = 11.9, 3.9$), 3.78 (2 H, m), 3.0 (1 H, br s), 2.5 (1 H, dd, $J = 11, 3.5$), 2.3 (1 H, d, $J = 11$), 0.08 (9 H, s); ^{13}C NMR (CDCl$_3$) δ 147.8, 146.2, 143.9, 141.9, 133.6, 133.3, 132.9, 129.7, 64.1, 44.6, 32.2, 1.0 (3C); HRMS (M + 1), calcd for $C_{14}H_{21}OSi$ 233.1361,

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2-(Trimethylsilyl)bicyclo[6.2.0]deca-2,4,6,8(1)-tetraen-10-methanol 3,5-Dinitrobenzoate (9). In a 10-mL flask was placed the alcohol from above (40 mg, 0.17 mmol) and 5 mL of dry dichloromethane followed by 3,5-dinitrobenzoyl chloride (46 mg, 0.2 mmol), triethylamine (0.1 mL, 0.7 mmol), and a catalytic amount of (dimethylamino)pyridine. The reaction mixture was stirred at room temperature for 1 h, diluted with 50 mL of dichloromethane, washed with water and brine, and dried over Na_2SO_4. The crude ester obtained after removal of the solvent was crystallized from petroleum ether–ethyl acetate to afford the crystalline 3,5-dinitrobenzoate derivative (70 mg) in 95% yield: mp 102.4 °C; IR (Nujol) 3050, 1720, 1630, 1590, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.23 (3 H, s), 5.93 (1 H, d, $J = 3.9$), 5.75 (1 H, dd, $J = 11.3, 4.3$), 5.59 (1 H, d, $J = 11.3$), 5.5 (1 H, dd, $J = 11.9, 3.9$), 5.4 (1 H, dd, $J = 11.9, 4.3$), 4.66 (2 H, m), 3.16 (1 H, m), 2.61 (1 H, dd, $J = 13.4, 4.5$), 2.35 (1 H, d, $J = 13.4$), 0.12 (9 H, s); UV (hexane) 210 nm, ϵ 45000; HRMS calcd for $C_{21}H_{22}N_2O_6Si$ 426.1241, found 426.1245. Anal. Calcd for $C_{21}H_{22}N_2O_6Si$: C, 59.14; H, 5.19; N, 6.57. Found: C, 59.09; H, 5.22; N, 6.53.

Electrochemistry. Electrochemical measurements were performed by using a BAS-100A electrochemical analyzer. The platinum working electrode was polished and rinsed with ethanol and acetone before each run. The counter electrode was platinum wire. The silver/silver nitrate reference electrode was made from silver wire and 0.1 M silver nitrate in HMPA and was isolated from the electrolyte by a VYCOR bridge. A 0.1 M solution of tetra-*n*-butylammonium perchlorate in HMPA was used as supporting electrolyte. Ferrocene/ferrocenium internal standard was checked against the reference before and after each measurement. A sample of **8** was weighed into the cell under argon. Supporting electrolyte (10 mL) was added via syringe to form a 1.5 mM solution of **8**.

Quenching Studies. Fluorescence emission spectra of biacetyl (2.6×10^{-2} M in benzene) in the presence of varying concentrations of quencher were recorded on an SLM 48000S spectrofluorometer with excitation at 403 nm. The integrated fluorescence intensity from 400 to 600 nm was used for Φ.

For quenching studies of the cycloaddition of **10** to give **11**, quencher in varying amounts was added to 3 mL of a 0.01 M degassed stock solution of **10** in acetonitrile containing adamantane. Samples were irradiated simultaneously in Pyrex tubes with a 450-W Hanovia lamp for 1.5 h. Samples were analyzed by capillary GC, and the relative amounts of the components were calculated by using the internal standard method.

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Supplementary Material Available: Tables of positional parameters, anisotropic displacement parameters, bond distances, bond angles, and torsional angles for **9** (9 pages); table of observed and calculated structure factors for **9** (18 pages). Ordering information is given on any current masthead page.

Evidence for Resonance-Assisted Hydrogen Bonding. 2.[1] Intercorrelation between Crystal Structure and Spectroscopic Parameters in Eight Intramolecularly Hydrogen Bonded 1,3-Diaryl-1,3-propanedione Enols

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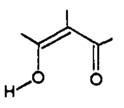
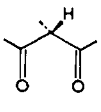
Abstract: Crystal structure analysis of eight 1,3-diaryl-1,3-propanedione enols has been accomplished with the aim of investigating in more detail the intramolecular hydrogen bond formed by the HO—C=C—C=O fragment characterizing β-diketone enols; structural data were correlated with spectroscopic parameters, that is IR ν(OH) stretching frequencies and ^1H NMR chemical shifts of the enolic proton. Present experimental data show that this hydrogen bond is characterized by the following interrelated features: (i) very short O- -O distances (2.432–2.554 Å); (ii) strong delocalization in the heteroconjugated fragment; (iii) lengthening of the O–H bond (to 1.20 Å); (iv) lowering of the ν(OH) frequencies (2566–2675 cm^{-1}) and downfield shift of the enolic proton resonance (15.3–17.0 ppm). The data can be interpreted by (and are in support of) the RAHB (resonance assisted hydrogen bond) model previously suggested (Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023) for explaining the unusual features the hydrogen bond displays in these compounds. It is shown that the model is able to interpret fine structural details such as the general weakening of the intramolecular hydrogen bond caused by electron-donating 1,3-substituents or additional hydrogen bonds accepted by the carbonyl and the preference displayed by the proton for dwelling on the carbonyl oxygen having the smaller negative charge induced both by the nature of 1,3-substituents or by intermolecular hydrogen bonds or short contacts.

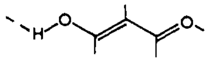
Structural chemistry of β-diketones has received increasing attention in the last few years.[1,2] The interest in the field arises from their being typical sample compounds for studying tautomerism in solution and from the fact that their enol form is stabilized by an intermolecular (Ic) or intramolecular (Id) hydrogen bond which has unusual characteristics. Furthermore, its energy contribution appears to be indispensable to the enolization process itself because, according to a variety of data collected by Emsley[2a] on malondialdehyde, the non-hydrogen-bonded enol form Ia is some 21 kJ mol^{-1} less stable than the diketone Ib. The role played by the hydrogen bond is such that, with very few exceptions,[3] and



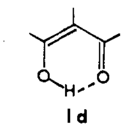
Ia



Ib



Ic



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[1] Part 1: Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023.

[2] (a) Emsley, J. *Struct. Bonding* **1984**, *57*, 147. (b) Etter, M. C.; Vojta, G. M. *J. Mol. Graphics* **1989**, *7*, 3. (c) Emsley, J.; Ma, L. Y. Y.; Bates, P. A.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Perkin Trans. 2* **1989**, 527. (d) Gilli, G.; Bertolasi, V. In *The Chemistry of Enols*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1990; Chapter 13.

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