# Benzoannulation as a Probe of Structural Dimension and π-Electron Distribution in Elassovalenes. A Mathematical Model for the Assessment of Homoaromaticity[1]

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Abstract: 6,7-Benzoelassovalene (5) has been synthesized from benzocyclobutene and 1,4-cyclohexadiene-1,2-dicarboxylic anhydride. This crystalline white solid undergoes rapid decomposition when exposed to air, but can be handled under an argon atmosphere. An x-ray crystal structure analysis of 5 is reported and the magnitudes of the nonbonded distances separating C_2–C_3 and C_{4a}–C_{8a} are revealed. These factors are considered in evaluating the possible neutral homoaromatic nature of the molecule. The preparation of 5,6-benzoelassovalene (3), an isomer of 5 which must maintain semibullvalene character to avoid disruption of benzenoid aromaticity, has also been completed. The lability of 3 exceeded that of 5 by a significant margin, and it unfortunately proved possible to characterize this compound only by mass spectrometry. NMR spectral data for 5 are presented, correlated with earlier findings, and analyzed in terms of a possible diamagnetic ring current. Lastly, a mathematical model has been devised which enables the magnitude of bonding interaction between homoaromatic centers to be evaluated.

Discovery of the clean electrocyclic rearrangement of semibullvalene 1 to 2 at temperatures below 30 °C has provided a most serviceable and efficient entry to the elassovalene ring system.[4,5] If orbital symmetry is controlling, this ring opening proceeds by disrotatory cleavage of the central norcaradiene σ bond with simultaneous π bond relocation within the developing cycloheptatriene moiety. Upon angular benzo fusion as in 3 (one valence tautomer illustrated), realization
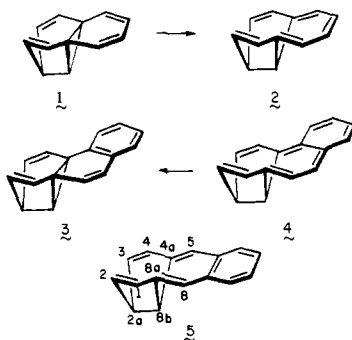
of a similar event is less likely, since disruption of benzenoid aromaticity would now be required (cf. 4).[6] Accordingly, this structural modification can be expected to result in maintenance of semibullvalenic character. For similar reasons, lateral benzo fusion as in 5 should guarantee adoption by the carbon network of the π-electronic features unique to 2.

Because annulation of a benzene ring to a fully conjugated $(4n + 2)$ cyclic π system is recognized to somewhat weaken the diamagnetic character intrinsic to the parent molecule,[7] the π bonds in 5 were expected to be more localized relative to 2. The homoaromatic character of the bridged cycloheptatriene unit[5,8,9] in 5 should accordingly be somewhat diminished, but the overall structural dimensions should not deviate greatly from those of 2. This is because the conformation of the elassovalene ring is fixed principally by the two mutually fused bridged carbons nearer the open end of the structure. In view of this projected close correspondence and anticipation of a crystalline nature for 5 suitable for detailed x-ray crystal structure analysis, its synthesis was deemed warranted. Our major goal was to establish the magnitudes of the nonbonded distances separating C_2–C_3 and C_{4a}–C_{8a}. Further experiments

reported here bear on the preparation of 3, an isomer of 5 which differs widely in its π-electronic constitution.

Synthesis of 5. The preparation of this hydrocarbon was based upon the now well-precedented[4,10] transformation of a [4.4.2]propella-2,4,11-triene such as 13 to a semibullvalene derivative (i.e., 17). Since a companion sequence for the efficient ring contraction of a cyclic anhydride to the requisite cyclobutene functionality was also available,[11] attention was directed initially to the preparation of 8 (Scheme I). The heating of benzocyclobutene (6), most conveniently prepared

Scheme I
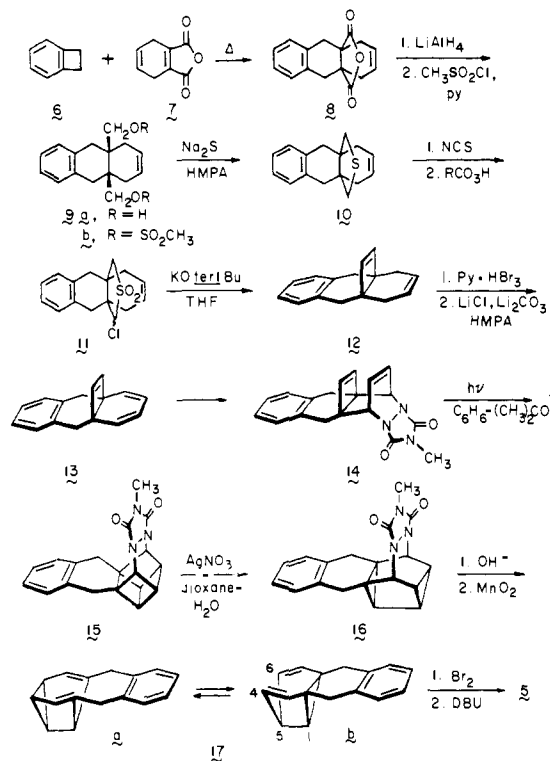
by the method of Sanders and Giering,[12] with 1,4-cyclohexadiene-1,2-dicarboxylic anhydride (7),[13] in toluene at 170 °C

(48 h, sealed tube) gave adduct **8** in 58% yield. The desired product could be readily separated from a bisadduct believed

18
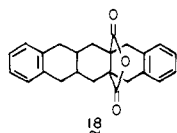
to possess structure **18** by simple sublimation. The relative yields of **8** and **18** were understandably related directly to the molar ratio of **6** to **7** which therefore had to be rather strictly controlled for our purposes (see Experimental Section). Conversion of **8** to sulfide **10**, followed by Ramberg–Bäcklund rearrangement,[14] led efficiently to **12**, bromination–dehydrobromination of which afforded **13**. The definitive ^{1}H NMR data for **13** (in CDCl$_3$) include an AB pattern for the cyclohexadiene ring centered at δ 5.76, a sharp cyclobutene singlet at 5.59, and a pseudosinglet for the four benzylic protons at 2.48. This unsaturated propellane reacted rapidly with N-methyltriazolinedione at −70 °C to give adduct **14**, the stereochemistry of which was established by intramolecular (2 + 2) cycloaddition under conditions of sensitized (benzene–acetone solution) irradiation. When exposed to a solution of silver nitrate in aqueous dioxane, resulting bishomocubane **15** underwent high yield isomerization[15] to **16**. Subsequent sequential treatment of **16** with hydroxide ion and manganese dioxide caused loss of the urazole ring with unmasking of two double bonds and generation of a semibullvalene nucleus.

The valence isomeric equilibrium prevailing in **17** was investigated by variable-temperature ^{1}H NMR studies in CS$_2$ solution at 100 MHz over the temperature range +27 to −94 °C. The closely related nonaryl fused system **19** is known to

a **19** **b**
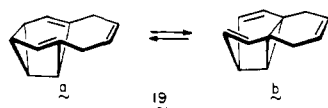
be characterized by a thermodynamically weighted preference for tautomer **b** having the cyclopropane ring positioned internally (74%, 40 °C, CDCl$_3$).[10c] Judging from the value of $\delta_{4,6}$ determined experimentally for the nonfluxional 2,8-pentamethylene derivative (5.59),[16] the readily computed mole fractions and equilibrium constants for the two rapidly equilibrating forms of **17** reveal that benzo annulation also acts on the energy of this extended semibullvalene framework to appreciably stabilize form **b** (96%, 27 °C, CS$_2$).[17] Since this equilibrium imbalance is only marginally sensitive to temperature (Table I), $\Delta H°$ probably approaches zero and $\Delta S°$ probably accounts for more than half of the magnitude of the $\Delta G°$ values throughout the range studied. Although changes in ground-state equilibria with changing T become difficult to measure accurately when one component dominates by 96–98%, the "bracketing effect" of an o-xylene unit clearly favors bonding to a cyclopropane ring rather than to a pair of olefinic carbons by 1.4–1.9 kcal/mol. The wider margin of preference for tautomer **b** in **17** relative to **19** is believed to be a reflection of the added inductive effect of the benzene ring.[10]

To achieve the requisite formal oxidation of **17**, the crystalline white solid was treated first with 1 mol equiv of bromine in dichloromethane solution. Dehydrobromination of the resulting dibromide mixture with 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) in tetrahydrofuran solution at 25 °C gave rise to benzoelassovalene **5** as expected. Although this substance can be obtained as a nicely crystalline white solid by recrystallization from deoxygenated methanol, it experiences rapid decomposition when exposed to the atmosphere. Slower resinification occurs upon storage in the cold. Its stability under

Table I. Variable-Temperature ^{1}H NMR Data (100 MHz, CS$_2$), Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values ($\Delta G°$) for the Fluxional System **17a** $\rightleftarrows$ **17b**[a]

Temp, °C	Chemical shift H$_4$,H$_6$ (δ)	Mol fraction **b** (10^2)	K_{eq} (a/b)	Ln K_{eq}	$\Delta G°$, cal/mol
27.0	5.46	96.0	0.042	−3.18	1900
−4.3	5.49	96.9	0.032	−3.45	1840
−34.3	5.51	97.5	0.025	−3.68	1750
−94.0	5.53	98.1	0.019	−3.97	1400

[a] The chemical shifts of the aromatic protons showed no comparable temperature dependence.

argon at room temperature is such, however, that it can be handled under conditions of this type.

Preparation of 3. Given the successful synthesis of **5** by elaboration of tetracyclic anhydride **8**, attention was next turned to **21** as a possible starting material for **3**. In fact, Diels–Alder addition of butadiene to conveniently available 3,4-dihydro-1,2-naphthalic anhydride (**20**)[18] according to the procedure of Fieser and Hershberg[19] was found to comprise a ready source of **21** (Scheme II). The conversion of **21** to **25**

Scheme II
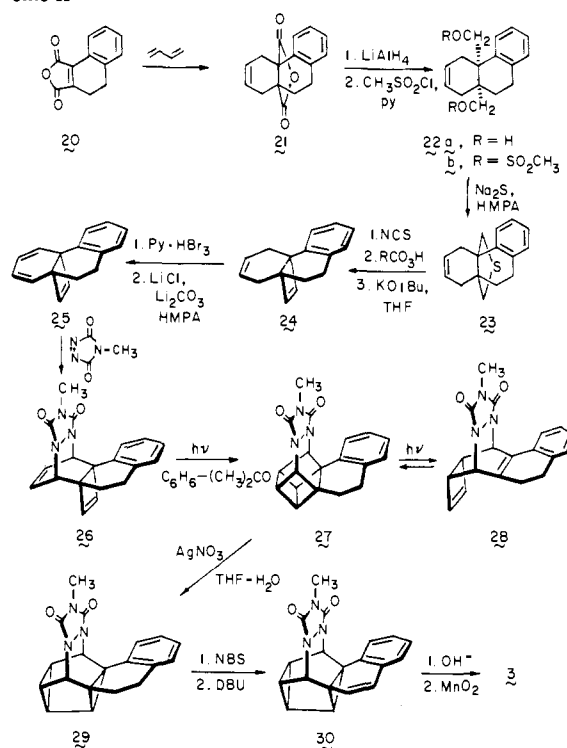
as modeled upon our prior work proceeded uneventfully. The unsymmetrical nature of this hydrocarbon was clearly revealed by its ^{1}H NMR spectrum (in CDCl$_3$) which displays a complex multiplet for the six olefinic protons in the region δ 6.34–5.52, a pseudosinglet for the cyclobutene pair at 5.84, and two upfield multiplets each of area 2 for the benzylic (2.78–2.56) and isolated methylene groups (2.01–1.22).

Addition of N-methyltriazolinedione to **25** at −70 °C afforded a singlet adduct. That entry of the dienophile had occurred from that surface anti to the cyclobutene ring was suggested by Eu(fod)$_3$-induced shifting experiments and substantiated by the photochemical behavior of **26**.

Irradiation of a benzene–acetone (1:1) solution of **26** through Corex with a 450-W Hanovia lamp for 3 h resulted in conversion to **27** (71%) and **28** (25%; yields based upon unconsumed **26** after silica gel chromatography). At shorter reaction times, the relative percentages of **28** were appreciably

Table II. Comparative ^{13}C NMR Chemical Shift Data (12.6 MHz, CDCl$_3$, ppm)

Carbon atoms	2	5
1,4	133.9[a]	132.1
2,3	115.0	117.9
2a	55.3	56.9
4a,8a	136.4	136.3
5,8	130.8[a]	125.2[b]
8b	46.4	45.1
6,7	127.5	145.7[c]
Remaining aryl		130.6, 137.9

[a] Interchangeable values. [b] Benzylic centers. [c] Quaternary aromatic carbons.

Table III. Selected Bond Distances for 6,7-Benzoelassovalene (5)[a]

Atom pair	Bond distance, Å	Atom pair	Bond distance, Å
C$_{4a}$-C$_5$	1.340(9)	C$_7$-C$_8$	1.446(10)
C$_4$-C$_{4a}$	1.431(11)	C$_8$-C$_{8a}$	1.329(9)
C$_{4a}$-C$_{8b}$	1.486(9)	C$_1$-C$_{8a}$	1.438(10)
C$_5$-C$_6$	1.456(10)	C$_{8a}$-C$_{8b}$	1.514(9)
C$_6$-C$_9$	1.401(10)	C$_1$-C$_2$	1.318(11)
C$_6$-C$_7$	1.433(10)	C$_2$-C$_{2a}$	1.515(11)
C$_9$-C$_{10}$	1.347(11)	C$_{2a}$-C$_3$	1.510(10)
C$_{10}$C$_{11}$	1.391(13)	C$_{2a}$-C$_{8b}$	1.533(10)
C$_{11}$-C$_{12}$	1.369(12)	C$_3$-C$_4$	1.334(12)
C$_7$-C$_{12}$	1.415(10)		

[a] The standard deviations appear in parentheses.

less. Since bishomocubane **27** independently undergoes photofragmentation to **28** under these conditions, it is seen to be the intermediate linking **28** to **26**.[20] Inasmuch as **27** is a diazabishomocubane, it was subject to efficient isomerization to **29** in the presence of Ag(I) ion.

Additional unsaturation was introduced into this diazasnoutane through benzylic bromination (NBS) and DBU-promoted elimination. Although this sequence has occasionally proven frivolous, it does comprise a quite usable route to **30** whose spectral features are sufficiently unique to permit unequivocal structural assignment (see Experimental Section). When samples of **30** were sequentially hydrolyzed and treated with manganese dioxide under conditions very carefully controlled to preclude adventitious exposure to oxygen, there could be obtained a particularly unstable off-white solid. Although it proved possible to obtain mass spectral evidence for the formation of **3**, all attempts to record ^{1}H NMR spectra resulted in rapid polymerization. Inasmuch as **3** decomposes rapidly under various inert atmospheres, its very marked lability appears not to be due only to a propensity for air oxidation. This substance clearly ranks as the most sensitive of the many semibullvalene derivatives prepared in this laboratory.

NMR Spectral Parameters of 5. In agreement with the symmetrical nature of 6,7-benzoelassovalene, its ^{1}H NMR spectrum is characterized by five signals in addition to those of the aryl protons. In accord with the anticipated reduction in π-electron mobility relative to the parent hydrocarbon, the resonance peaks for H$_{2a}$ and H$_{8b}$ are shifted downfield relative to those in **2**. Although H$_{8b}$ (δ 2.57 vs. 1.78) is likely deshielded to an additional extent by virtue of its position relative to the fused benzene ring, H$_{2a}$ ($\delta \sim 4.0$ vs. 3.77) clearly cannot be comparably affected. The chemical shift difference ($\Delta\delta = 0.23$) of the latter proton suggests that an electronic perturbation may have occurred as well at the "open end" of the structure upon benzoannulation.

The emergent patterns for H$_2$ and H$_2$ in **5** indicate that the vicinal coupling constants $J_{1,2}$ (5.5 Hz) and $J_{2,2a}$ (2.5 Hz) compare favorably with those of **2**. The chemical shift of H$_1$ (δ 6.43 vs. 6.45) has remained unchanged, while that of H$_2$ (6.17 vs. 6.02) is positioned somewhat more downfield. The newly acquired benzylic character of the remaining olefinic hydrogen (H$_8$) expectedly causes this signal to be downfield shifted by 0.26 ppm.

A comparison of the ^{13}C NMR shifts of the individual carbon atoms in **2** and **5** is made in Table II. Clearly revealed therein is the fact that peripheral carbons 1-4, 4a, and 8a, as well as the tetrahedrally hybridized apical carbons 2a and 8b compare very closely. As previously discussed,[5,21] such correspondence does not comprise a suitable probe for the magnitude of a possible diamagnetic ring current in the elassovalene frame. Nor does it necessarily signal the presence of homoconjugative interaction. However, the data do reveal the existence of a close conformational relationship between **2** and

5 such that the prevailing steric contributions to the relevant ^{13}C shifts are similar. In the section which follows, the precise three-dimensional features of the carbon skeleton in **5** has been determined by x-ray diffraction. The combination of these experimental techniques shall in turn allow us to comment upon the molecular geometry of **2**.

X-Ray Crystal Structure Analysis. Crystals of **5**, grown by slow cooling of a CH$_3$OH solution to -20 °C in an inert atmosphere, were placed in Lindemann capillaries which were then sealed in an inert atmosphere. Preliminary photographs reveal monoclinic symmetry. Accurate cell constants were obtained from a least-squares fit of 15 high angle reflections whose θ values were measured on a four-circle diffractometer. At ambient temperature the cell constants were $a = 10.586$ (1), $b = 34.246$ (3), $c = 6.285$ (1) Å and $\beta = 99.31$ (1)°. The sensitivity of the molecule precluded a density measurement. The systematic extinctions conformed to space group $P2_2/c$, and a plausible calculated density of 1.21 g/cm^3 for $Z = 8$ was taken to indicate that *two* molecules of C$_{16}$H$_{12}$ formed the asymmetric unit.

All unique diffraction maxima with $2\theta \leq 114.1$° were measured on a computer-controlled four-circle diffractometer using graphite monochromated Cu Kα (1.54178 Å) radiation and a θ-2θ scan. A total of 3114 diffraction maxima were measured in this fashion of which only 1212 (39%) were considered observed ($I \geq 2\sigma(I)$) after correction for Lorentz, polarization, and background effects. Efforts to improve the scattering by recollecting data at ~ -120 °C were not successful; essentially the same data were obtained.

The angular dependence of the reflections was removed and the latter were converted to normalized structure factors.[22] Signs were given to the 300 largest E's with a multisolution, weighted sign determining procedure. The E synthesis showed the structure of one molecule of **5** quite clearly but the other molecule was not at all clear. One molecule of the benzoelassovalene appears to be statistically disordered about a pseudo-twofold axis perpendicular to the molecular plane. Full-matrix least-squares refinements with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for hydrogen have converged to a conventional discrepancy index of 0.072.[23] In this model one molecule of **5** is well behaved and the other fragment has 18 independent atoms representing the disordered molecule. Atoms C$_{2a}$ and C$_{8b}$ had to be put in with 50% occupancy, and both sides of the molecule and the peripheral atoms appeared at averaged positions. In a second model, used to check the correctness of our interpretation, the disordered molecule was approximated by two molecules of **5** and the parameters were obtained from the ordered molecule. All molecules were then required to refine as rigid groups. The conventional crystallographic discrepancy index for this model was 0.079.

The resultant bond distances and angles for **5** are compiled in Tables III and IV, and a computer-generated perspective drawing of the hydrocarbon is given in Figure 1. The final

Table IV. Selected Bond Angles for 6,7-Benzoelassovalene (5)[a]

Atom triple	Angle, deg	Atom triple	Angle, deg
C(4)–C(4a)–C(5)	129.2(7)	C(7)–C(8)–C(8a)	127.4(8)
C(5)–C(4a)–C(8b)	123.1(7)	C(1)–C(8a)–C(8)	128.3(8)
C(4)–C(4a)–C(8b)	107.7(8)	C(8)–C(8a)–C(8b)	123.5(7)
C(4a)–C(5)–C(6)	128.0(7)	C(1)–C(8a)–C(8b)	108.2(7)
C(5)–C(6)–C(9)	118.2(8)	C(2)–C(1)–C(8a)	110.5(9)
C(5)–C(6)–C(7)	122.6(7)	C(2)–C(2a)–C(3)	114.5(7)
C(7)–C(6)–C(9)	119.0(8)	C(2)–C(2a)–C(8b)	102.7(7)
C(6)–C(9)–C(10)	122.4(9)	C(3)–C(2a)–C(8b)	102.9(7)
C(9)–C(10)–C(11)	120.3(1.0)	C(2a)–C(3)–C(4)	111.5(9)
C(10)–C(11)–C(12)	118.7(1.0)	C(3)–C(4)–C(4a)	111.6(8)
C(7)–C(12)–C(11)	123.6(9)	C(4a)–C(8b)–C(8a)	109.0(6)
C(6)–C(7)–C(12)	115.9(8)	C(2a)–C(8b)–C(4a)	106.3(6)
C(6)–C(7)–C(8)	124.7(7)	C(2a)–C(8b)–C(8a)	105.2(6)

[a] The standard deviations appear in parentheses.

Figure 2. Schematic representation of the hydrocarbon geometry showing averaged bond lengths and torsional angles.

—— Increasing σ Contribution ——→

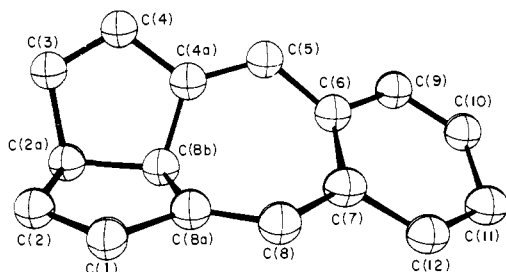**Figure 3.** Different geometrical orientations of p orbital pairs.

Figure 4.

Figure 1. A computer-generated perspective drawing of 5. Only the ordered molecule is shown and hydrogen atoms are omitted.

fractional coordinates together with the observed and calculated structure factors may be found in the Supplementary Material. For the undisordered molecule, the estimated errors are 0.01 Å and 1° for bond distances and angles, respectively, as judged both from the variance–covariance matrix and from comparison of chemically identical but crystallographically distinct portions. The relatively low level of accuracy is attributable to the poor scattering of the crystals we were able to obtain for the x-ray experiment. Nevertheless, the molecule was clearly seen to possess mirror symmetry within experimental error and some interesting structural features were revealed.

As displayed in Figure 2, the average bond lengths argue quite convincingly for a predominantly localized structure, although the relatively short C_4-C_{4a} bond length (1.434 Å) and the C_3-C_4-C_{4a}-C_5 torsional angle (176°) are seen to be rather unusual. Furthermore, the p orbitals on C_4 and C_{4a} appear somewhat better aligned for overlap, as judged by the dihedral angles, than the formally doubly bonded carbons C_{4a} and C_5 where the torsional angle is 172°. The crucial C_{4a}-C_{8a} and C_2-C_3 distances are 2.44 and 2.54 Å, respectively. The internal gap in 5 compares rather closely with the transannular distances in 4,10-dibromo-1,7-methano[12]annulene (2.418 Å),[24] 2-hydroxy-4,9-methano[11]annulenone (2.309 Å),[25] and the bicyclo[5.4.1]dodecapentaenylium cation (2.299 Å).[26] All of these distances are unquestionably too long for *normal* π-π bonding overlap. For structural reasons, however, the pπ orbitals on the bridgehead carbons of these buckled molecules are canted to positions where one lobe is projected to some point on the interior of the concave surface. Therefore, to answer the critical question of whether transannular overlap with resultant homoconjugative interaction is operative, one should fully evaluate each system by vector analysis.

Discussion

Many of the recent concepts dealing with novel forms of extended conjugation such as homoaromaticity,[27] bicycloaromaticity,[28] spiroconjugation,[29] perpendicular orientation,[30]
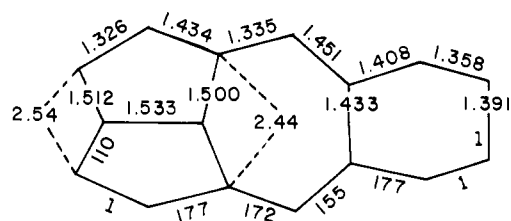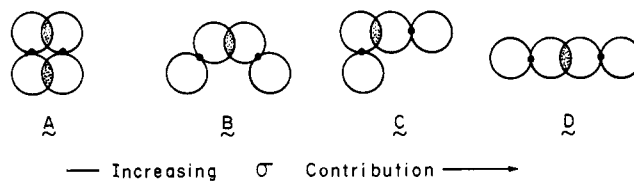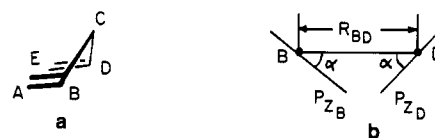
subjacent orbital control,[31] and ribbon topology[32] focus attention on the level of electronic interaction which may or may not result from a particular arrangement of p orbitals. When such orbitals are aligned in the well-known parallel combinations given by **A**, the resultant pp-π combination possesses a node in the plane of the bond axis and has angular momentum about this axis. As their spatial orientation is progressively altered to give arrangements such as **B** and **C** (Figure 3), a diminution in the level of π interaction and a concomitant increase in σ contributions to the bond energy can be expected to result (a fixed internuclear separation is assumed). At the far extreme, that particular combination of parallel colinear atomic orbitals depicted in **D** is seen to be cyclindrically symmetrical about the bond axis and to lack angular momentum about the internuclear axis. The marked contrast with **A** is obvious. We refer to the phenomenon illustrated by **D** as *pp-σ overlap*. With the notable exception of diazabicyclo-[2.2.2]octane,[33] there exists a dearth of organic molecules (particularly ionic systems) synthesized with the specific intent of completely factoring out the commonly prevailing π contributions to p orbital interaction, thereby enabling study of pure pp-σ interactive behavior.[34]

When 6,7-benzoelassovalene (5) is viewed from its basal plane, a cross section reveals the C_{4a}-C_{8a} and C_2-C_3 p lobes to be geometrically related as in **B**. Since this is a state of interaction intermediate between pp-π and pp-σ, the extent of transannular bonding in 5 should be a function of the particular linear combination of the two pure interactions (in turn directly dependent upon the interorbital dihedral angle) and the prevailing distance separating them. For such homoaromatic systems, an evaluation of bonding interaction between the carbon atoms surrounding the gap (labeled as B and D in Figure 4a) would ideally be realized by a detailed molecular orbital calculation of a type which would simultaneously yield the ground-state molecular wave function and a complete bond-order profile. But this would be inordinately expensive, at least at the present time. However, as we shall demonstrate, it is possible to estimate by a rather simple calculation the extent of interpenetration of the opposed p_z orbitals of atoms B and D and thus the maximum of the possible bonding interaction between these centers.

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For this purpose, we require only the internuclear distance (R_{BD}) and the orientations of the two p orbitals, one each from B and D, relative to the internuclear vector $\vec{R}_{BD}$ and each other (Figure 4b). The extent of interpenetration is given by the overlap integral, over all space, of the p-orbital wave functions:

$$S(p_{z_B}, p_{z_D}) = \int \psi 2p_{z_B} \psi 2p_{z_D} \, d\tau$$

Analytical parameterized solutions for integrals of this type have been generated by Mulliken for Slater orbitals.[35] Modification of these solutions for our particular symmetric geometry (see Appendix) yields the exact analytic solution for the overlap integral in terms of the dimensionless parameter $P = \mu_c R_{BD}/a_0$ and the angle α (which lies between the p-orbital direction and the internuclear vector $\vec{R}_{BD}$).

$$S(p_{z_B}, p_{z_D}) = e^{-P} \left\{ \sin^2 \alpha \left(1 + P + \frac{2}{5}P^2 + \frac{1}{15}P^3 \right) \right.$$
$$\left. - \cos^2 \alpha \left(1 + P + \frac{1}{5}P^2 - \frac{2}{15}P^3 - \frac{1}{15}P^4 \right) \right\}$$

R_{BD} is again simply the internuclear distance in ångströms, μ_c is the Slater radial exponent term for carbon (1.625), and a_0 is the Bohr radius for hydrogen (0.529 Å). Implicit in this calculation are the assumptions that the orbitals are pure p in nature and that we can define their directions accurately.

For the examples assessed here, viz., 1,4,7-cyclononatrienes (31),[36] triquinacene (32),[37] and 5, the double bonds A=B and

D=E are well localized, with distances characteristic of essentially pure sp^2-sp^2 σ bonds and p_z-p_z π bonds. This is further supported by the coplanarity of the C—C=C—C groupings, as measured by torsion angle and least-squares plane calculations. We can therefore safely assume that the p_z orbital of atom B is in each case coaxial with the normal, at B, to the plane defined by atoms A-B-C. The direction cosines (with respect to an orthonormal coordinate system) of this normal vector are readily calculable from the interatomic vectors $\vec{R}_{AB}$ and $\vec{R}_{BC}$, and the angle α is simply obtained by taking the vector dot-product of the normal and $\vec{R}_{BD}$.[38]

It must be borne in mind that the value for an overlap integral can only give the maximal extent of interaction of the two orbitals because they may not be fully occupied. The latter situation may arise, for example, if the atomic orbital in question is not a dominant contributor to the molecular wave functions comprising the ground-state configuration for the molecule. Also, there must be some assurance that the two p_z orbitals have the same phase in the overlap region so that their interaction is positive (bonding) rather than negative (antibonding). The high degree of localization of the double bonds supports the full occupancy, while the theoretical and photoelectron spectroscopic data[39-41] provide convincing evidence of the proper symmetry of these orbitals.

In Table V are summarized our computational determinations of the overlap integrals for each of the structural arrangements generalized in Figure 4 which prevail in 5, 31, and 32. Comparison of these values with the overlap of the central (sp^2-sp^2) bond in biphenyl reveals the formal bond orders to be something less than 0.1 for the "bond" between atom pairs B and D. The values of the overlap integrals are small because the internuclear distances are quite large compared to normal bond distances. The overlaps occur only at the periphery of the p_z orbitals where the probability density is low and changing slowly with distance from the nucleus. The differences between 5, 31, and 32 are, however, considerable, up to 20% of the size

Table V. Computed Overlap Integrals

Compd	R_{BD}, Å	α, deg	S_{BD}
1,4,7-Cyclononatriene (31)[a]	2.464	54.18	0.066
Triquinacene (32)[b]	2.533	59.18	0.054
6,7-Benzoelassovalene (5)			
C_{4a}–C_{8a}	2.440	58.91	0.061
C_2–C_3	2.546	59.32	0.050
Cycloheptatriene[c]	2.511	67.42	0.042
Biphenyl (sp^2)	1.520	0.0	0.687

[a] Data taken from ref 36. [b] Data taken from ref 37. [c] Data taken from M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

of the interaction, sufficient to explain the direction and order of magnitude of the photoelectron spectroscopy results.

In 31, the observed 0.9-eV split between the degenerate highest occupied and lowest molecular π orbitals indicates the resonance integral for homoconjugative interaction to be 0.3 eV.[39] In 32, the lessened split (0.35-0.4 eV)[40] reveals the lower limit of the resonance integral between the π orbitals to be 0.1 eV. This value is a lower limit because hyperconjugative interactions in triquinacene seemingly destabilize the lowest π orbital causing the split to be smaller than it would be if through-space conjugation interactions operated exclusively. Notwithstanding, the diminished homoconjugation in 32 relative to 31, as enforced by the differing molecular topologies,[36,37] falls quantitatively in line with the respective overlap integrals (S_{BD}, Table V). When these criteria are applied to 6,7-benzoelassovalene (5), there is seen to exist a close correspondence between the interaction in the central portion of the molecule ($S = 0.061$) and that in 1,4,7-cyclononatriene ($S = 0.066$). Furthermore, the overlap integral for the C_2-C_3 interaction ($S = 0.050$) is rather closely aligned with that for triquinacene ($S = 0.054$). We interpret this as a reflection of comparable levels of homoconjugative interaction in 31 and the cycloheptatriene moeity in 5. The much smaller overall interaction across the open end of 5 is probably at the limit of detectability as in the case of triquinacene.

It follows from these conclusions that mutually canted homoconjugated carbon atoms can still interact significantly when separated by internuclear distances as large as 2.45 Å. It is perhaps appropriate in closing to draw attention to more conventional phenomena where interatomic distances are known with comparable accuracy. Thus, the normal intermolecular distance between stacked aromatic nuclei in crystals has been recognized for some time to be 3.40 Å.[42] At this distance, π-π repulsions appear to be comfortably avoided. However, in molecules such as [2.2]metacyclophane, [2.2]paracyclophane, and tetradehydro[2.2]paracyclophane where structural constraints cause π-π repulsions to gain major importance,[43] the closest approaches of the two benzene rings to one another have been experimentally determined to be 2.69,[44] 2.78,[45] and 2.80 Å, respectively.[46] These distances are uniformly larger than those prevailing at the key sites in 5, 31, and 32. That homoconjugative interactions can operate at these distances is therefore not surprising. The challenge which lies ahead is the construction of novel new unsaturated alicyclic molecular topologies having nonconjugated π-π overlap intergrals greater than those presently determined for 5, 31, and 32 (Table V).

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, Varian HA-100, and Bruker HX-90 spectrometers; the latter instrument was used to record the ^{13}C spectra. Apparent splittings are given. Infrared spectra were determined on Perkin-Elmer Model 127 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by

the Scandinavian Microanalytical Laboratory. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

2,3-Benzo-$\Delta^{2,6}$-hexalin-9,10-dicarboxylic Anhydride (8). A mixture of 5.0 g (48 mmol) of benzocyclobutene (6),[12] 5.0 g (33.3 mmol) of 1,4-cyclohexadiene-1,2-dicarboxylic anhydride (7),[13] and 10 mL of toluene was heated in a sealed tube at 170 °C for 48 h in a rocking autoclave. The cooled contents of the tube were transferred to a round-bottom flask and the toluene was evaporated in vacuo. The residue was sublimed (150 °C 0.1 mm)) to give 4.9 g (58%) of the monoadduct 8, mp 149–150 °C (from ether); $\delta_{TMS}^{CDCl_3}$ 7.12 (s, 4), 5.97 (m, 2), 2.96 (ABq, 4), and 2.45 (ABq, 4); m/e 254.0947 (calcd 254.0943).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.28; H, 5.66.

The residue from the sublimation was washed with ether and dried to give 4.8 g of bisadduct 18, mp 215–220 °C; $\delta_{TMS}^{CDCl_3}$ 7.08 (br s, 8) and 3.22–1.43 (m, 14); m/e 358.1574 (calcd 358.1569).

cis-9,10-Bis(hydroxymethyl)-2,3-benzo-$\Delta^{2,6}$-hexalin (9a). To a slurry of 11.4 g (0.30 mol) of lithium aluminum hydride in 300 mL of anhydrous tetrahydrofuran was added dropwise under nitrogen a solution of 47.9 g (0.19 mol) of anhydride 8 in 300 mL of tetrahydrofuran. After the addition was complete the reaction mixture was heated at reflux for 20 h, cooled in an ice–water bath, and treated sequentially with 12 mL of water, 9 mL of 20% sodium hydroxide solution, and 42 mL of water. The inorganic salts were removed by suction filtration and washed with two 250-mL portions of tetrahydrofuran. Evaporation of the combined filtrates gave after vacuum drying 43.3 g (96%) of diol 9a, mp 103–104 °C (from benzene–hexane); $\delta_{TMS}^{CDCl_3}$ 6.92 (s, 4), 5.47 (m, 2), 4.60 (br s, 2), 3.52 (s, 4), 2.73 (s, 4), and 2.02 (m, 4); mass spectrum: no molecular ion, strong P − 18 and P − 36 peaks.

cis-9,10-Bis(methanesulfonyloxymethyl)-2,3-benzo-$\Delta^{2,6}$-hexalin (9b). In a three-necked, 500-mL, round-bottomed flask equipped with a mechanical stirrer, a thermometer, and an addition funnel was placed 100 ml of pyridine. The reaction flask was cooled in a dry ice–carbon tetrachloride bath. To the cold pyridine was added in one portion 52.2 (0.455 mol) of methanesulfonyl chloride. A solution of 43 g (0.176 mol) of diol 9a in 150 mL of pyridine was added at such a rate that the temperature remained below −10 °C. After the addition was complete, the reaction mixture was stirred at 0 to −10 °C for 3 h, treated with 6 mL of water, and carefully poured into 700 mL of cold 4 N hydrochloric acid. After 30 min, the aqueous layer was decanted and the gummy, tan-colored residue was dissolved in a minimal amount of acetone. Water was added to the acetone solution until cloudiness persisted. After precipitation had begun an additional 700 mL of water was added. The precipitate was collected by suction filtration and dried in a vacuum desiccator to give 67.2 g (95%) of 9b, mp 161–162 °C (from methanol–chloroform); $\delta_{TMS}^{CDCl_3}$ 7.12 (s, 4), 5.67 (m, 2), 4.30 (s, 4), 2.94 (s, 6) 2.87 (s, 4), and 2.17 (m, 4).

Anal. Calcd for $C_{18}H_{24}O_6S_2$: C, 53.98; H, 6.04. Found: C, 53.84; H, 6.09.

3,4-Benzo-12-thia[4.4.3]propella-3,8-diene (10). In a 1-L, three-necked, round-bottomed flask equipped with a capillary tube, mechanical stirrer, and 60° adapter with condenser, vacuum adapter, and receiving flask were placed 141 g (0.59 mol) of sodium sulfide nonahydrate (recrystallized from 95% ethanol) and 750 mL of hexamethylphosphoramide (HMPA). The mixture was vacuum distilled at 20 mm until 120 mL of distillate had been collected and cooled to room temperature. The distillation apparatus was replaced by a reflux condenser fitted with a nitrogen inlet and the capillary tube was replaced by a thermometer. To this sodium sulfide–HMPA mixture was added 78.5 g (0.196 mol) of 9b in one portion. The resulting mixture was heated at 120 °C with stirring under nitrogen for 20 h, cooled, and diluted with 2.5 L of water prior to extraction with ether (5 × 250 mL). The combined extracts were washed with water (2 × 250 mL), dried, and evaporated. The residue was chromatographed on alumina (hexane elution) to give 35.0 g (74%) of 10, mp 65–67 °C (from benzene–hexane); $\delta_{TMS}^{CDCl_3}$ 6.98 (s, 4), 5.47 (m, 2), 2.83 (ABq, 4), 2.80 (s, 4), and 2.13 (m, 4); m/e 242.1133 (calcd 242.1129).

The sulfide was further characterized as the corresponding sulfone (obtained by monoperphthalic acid oxidation), mp 151–215 °C (from ethanol); $\delta_{TMS}^{CDCl_3}$ 7.11 (s, 4), 5.66 (m, 2), 3.14 (s, 4), 3.02 (ABq, 4), and 2.32 (m, 4).

Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 69.98; H, 6.61.

3,4-Benzo-11-chloro-12-thia[4.4.3]propella-3,8-diene 12,12-Dioxide (11). A mixture of 34.0 g (0.14 mol) of 10, 19.2 g (0.144 mol) of N-chlorosuccinimide, and 400 mL of carbon tetrachloride was refluxed under nitrogen for 3 h. The reaction mixture was cooled and the precipitated solid was removed by suction filtration. The filtrate was evaporated to give α-chloro sulfide as a pale yellow oil; $\delta_{TMS}^{CDCl_3}$ 7.04 (s, 4), 5.53 (m, 2), 5.47 (s, 0.5), 5.37 (s, 0.5), and 3.47–2.08 (m, 10). The mixture of isomers was used without further purification.

To a solution of the chloro sulfides in 400 mL of ether cooled in a dry ice–carbon tetrachloride bath was added dropwise 264 mL (0.28 mol) of 1.02 M monoperphthalic acid in ether. After the addition was complete the reaction mixture was stirred at room temperature overnight. The precipitated phthalic acid was removed by suction filtration and the filtrate was washed with 0.5 N sodium hydroxide solution (2 × 200 mL) and brine (2 × 200 mL) prior to drying and solvent evaporation. The last traces of solvent were removed under high vacuum to give a mixture of chloro sulfones as a foamy, white solid, mp 56–82 °C; $\delta_{TMS}^{CDCl_3}$ 7.03 (s, 4), 5.57 (m, 2), 5.03 (s, 0.5, >CHCl of one isomer), 4.87 (s, 0.5, >CHCl of other isomer), and 3.67–2.13 (m, 10); m/e 308.0642 (calcd 308.0638). This mixture was used without further purification.

3,4-Benzo[4.4.2]propella-3,8,11-triene (12). To the α-chloro sulfone mixture of 11 in 500 mL of anhydrous tetrahydrofuran cooled in a dry ice–carbon tetrachloride bath under nitrogen was added in one portion 87.5 g (0.78 mol) of potassium *tert*-butoxide. The mixture was stirred at −20 °C for 30 min and subsequently heated to reflux for 2.5 h. The slurry was cooled, diluted with 2 L of water, and extracted with pentane (4 × 250 mL). The combined pentane extracts were washed with water, dried, and evaporated to give an oil which was purified by chromatography on alumina (pentane elution). The yield of 12 was 20.1 g (69% from 10). The analytical sample was obtained by preparative VPC (2 ft × 0.25 in. 8% SE-30 on Gas Chrom P, 160 °C) followed by sublimation, mp 52–53 °C; $\delta_{TMS}^{CDCl_3}$ 7.05 (s, 4), 5.77 (m, 2), 5.60 (s, 2), 2.62 (s, 4), and 2.09 (m, 4); m/e 208.1254 (calcd 208.1252).
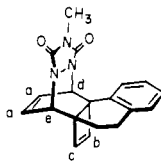
Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.76.

3,4-Benzo[4.4.2]propella-3,7,9,11-tetraene (13). A mixture of 18.3 g (0.088 mol) of 12, 29.6 (0.0925 mol) of pyridinium hydrobromide perbromide, 300 mL of glacial acetic acid, and 300 mL of carbon tetrachloride was stirred at room temperature for 3 h. The solution was diluted with 600 mL of water and the layers were separated. The aqueous phase was extracted with carbon tetrachloride (3 × 200 mol). The organic layer was combined with the extracts and washed with water (2 × 200 mL), 0.5 N sodium hydroxide solution (2 × 200 mL), and again with water (2 × 200 mL) prior to drying and evaporation. There was obtained 28.0 g (86.5%) of dibromide, mp 120–123 °C; $\delta_{TMS}^{CDCl_3}$ 7.03 (s, 4), 6.02 (d, $J = 3$ Hz, 1), 5.62 (d, $J = 3$ Hz, 1), 4.87–4.35 (m, 2), and 2.61–1.83 (m, 8); m/e 365.9624 (calcd 365.9620).

To a solution of 27.5 g (0.075 mol) of crude dibromide in 500 ml of anhydrous HMPA under nitrogen was added in one portion 31.8 g (0.75 mol) of anhydrous lithium chloride and 55.5 g (0.75 mol) of anhydrous lithium carbonate. The resulting mixture was stirred at 85–90 °C for 24 h, cooled to room temperature, and diluted with 2.5 L of water. The solution was extracted with pentane (4 × 500 mL) and the combined extracts were washed with water (4 × 200 mL), dried, and evaporated to leave a dark-colored oil. Chromatography on alumina (pentane elution) gave 12.5 g (81%) of 13. An analytical sample was prepared by preparative VPC (2 ft × 0.25 in. 8% SE-30 on Gas Chrom P, 160 °C) followed by sublimation (50 °C (0.01 mm)); mp 57 °C; $\delta_{TMS}^{CDCl_3}$ 7.06 (br s, 4), 5.76 (ABq, 4), 5.59 (s, 2), and 2.48 (s, 4); m/e 206.1099 (calcd 206.1095).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.13; H, 6.81.

5,8-Dihydro-N-methyl-1,4:4a,8a-diethenobenzo[g]phthalazine-2,3(1H,4H)-dicarboximide (14). To a solution of 12.5 g (0.060 mol) of 13 in 300 mL of ethyl acetate–pentane (4:1) cooled in a dry ice–isopropyl alcohol bath was added dropwise a saturated solution of N-methyltriazolinedione in ethyl acetate until a light pink color persisted. The resulting solution was allowed to stand at room temperature for 1 h before the precipitated adduct was collected by suction filtration and dried (14.7 g). The filtrate was evaporated and the residue was washed with ether to give an additional 2.8 g of 14 (total yield of 90.4%). The analytical sample was prepared by recrystallization from absolute ethanol), mp 245–246 °C; $\delta_{TMS}^{CDCl_3}$ 7.13 (s, 4), 6.22 (m, 2), 5.66 (s, 2), 4.74 (m, 2), 3.02 (s, 3), and 2.99 (ABq, 4); m/e

Table VI. Eu(fod)₃ Shift Study of Adduct 26

Eu(fod)₃, %	Chemical shifts, δ					
	H_a	H_b	H_c	H_d	H_e	CH_3
0	6.29	6.01	5.74	5.50	4.70	2.92
5	6.37	6.02	~5.85	5.80	5.14	3.33
10	6.48	6.07	5.84	6.17	5.62	3.58
15	~6.57	~6.10	5.90	~6.57	~6.10	3.92
20	~6.68	6.15	5.97	~6.82	~6.58	4.17

319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16. Found: C, 71.45; H, 5.37; N, 12.89.

Photocyclization of 14. A solution of 1.00 g (3.13 mmol) of **14** in 400 mL of benzene–acetone (1:1) was irradiated for 1 h with a 450-W Hanovia lamp through Corex. Six such reaction mixtures were combined, evaporated, and chromatographed on silica gel (ether elution) to remove the aldol products (from acetone). A solvent polarity increase to ether–chloroform (1:1) served to elute 5.58 g (93%) of **15**, mp 219–220 °C (from ethanol); $\delta_{TMS}^{CDCl_3}$ 7.17 (m, 4), 4.73 (m, 2), 3.76–3.38 (m, 2), and 2.95–2.79 (m with s at 2.87, 9); m/e 319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16. Found: C, 71.10; H, 5.41; N, 13.25.

Ag⁺-Catalyzed Rearrangement of 15. A mixture of 0.60 g (1.88 mmol) of **14**, 9.57 g (56.4 mmol) of silver nitrate, and 75 mL of dioxane–water (4:1) was heated in a sealed tube at 100 °C for 36 h. The reaction mixture was cooled, filtered through Celite, and evaporated. The residue was extracted with chloroform (4 × 15 mL) and the combined extracts were washed with water (2 × 15 mL) and brine (2 × 15 mL) prior to drying and evaporation. There was obtained 0.55 g of yellowish product, chromatography of which on silica gel (chloroform elution) gave 0.50 g (83%) of **15**, mp 229–231 °C (from ethanol); $\delta_{TMS}^{CDCl_3}$ 7.05 (m, 4), 4.90 (m, 2), 3.09 (m, 4), 3.03 (s, 3), 216–1.92 (m, 3), and 1.83–1.70 (m, 1); m/e 319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16. Found: C, 71.13; H, 5.44; N, 12.99.

Annulated Semibullvalene 17. A mixture of 400 mg (1.25 mmol) of **16** and 2.00 g (50 mmol) of sodium hydroxide in 100 mL of isopropyl alcohol (note: *all* solvents were purged with argon prior to use) was refluxed under argon for 1 h. The solution was cooled to 0 °C, acidified to pH with 50% acetic acid, stirred for 15 min, and lastly basified with 3 M ammonium hydroxide solution to pH 9. To this solution were added 50 mL of pentane and 6.0 g of manganese dioxide (Attenburrow).[47] The reaction mixture was stirred under argon at room temperature overnight, filtered through Celite, and diluted with water (250 mL). The layers were separated (note: the semibullvalene solutions must be kept under an argon atmosphere at all times), the aqueous phase was extracted with pentane (4 × 75 mL), and the combined pentane extracts were washed with water (4 × 100 mL). The aqueous layer was combined with the washings and reextracted with pentane (3 × 75 mL). The second combined pentane extracts were washed with water, combined with the first pentane extracts, dried, and evaporated. Failure to back extract results in diminished yields. Sublimation of the residue (45 °C (0.6 μ)) gave 175 mg (68%) of **17**, mp 76–77 °C; $\delta_{TMS}^{CDCl_3}$ (60 MHz, 27 °C) 7.08 (m, 4), 5.67–5.52 (m, 2), 5.23 (d with further splitting, 2) 3.55 (m, 4), 3.36–3.15 (m, 1), and 2.42 (d with further splitting, 1); $\delta_{TMS}^{CS_2}$ (100 MHz, 27 °C) 6.97 (s), 5.46 (dd, J = 5 and 2 Hz), 5.10 (d, J = 5 Hz), 3.44 (br d, J = 5 Hz), 3.29–3.09 (m), 2.29 (br d, J = 6 Hz); ^{13}C NMR (CDCl₃): 135.75, 128.57, 126.90, 126.31, 125.44, 57.78, 54.01, 51.42, and 32.48 ppm; m/e 206.1091 (calcd 206.1095).

6,7-Benzoelassovalene (5). To a cold (−78 °C) solution containing 160 mg (0.775 mmol) of pure **17** and 0.3 mL of triethylamine in 30 mL of dichloromethane (note: all solvents were purged with argon before use) was added dropwise a solution of 124 mg (0.775 mmol) of bromine in 10 mL of dichloromethane. The mixture was stirred for an additional 30 min before solvent removal on a rotary evaporator (cold water bath). The residue was dissolved in 40 mL of tetrahy-

drofuran under argon, treated with 600 mg of diazabicycloundecene (DBU), and stirred at room temperature for 2 h. The solvent was removed, the residue was treated with 250 mL of water, and the resulting solution was extracted with pentane (4 × 50 mL). All operations were conducted under an argon atmosphere as much as possible. The pentane extract was washed with water (4 × 50 mL), the washings were reextracted with pentane (3 × 50 ml), and the combined pentane extracts were dried and evaporated. The crystalline residue was sublimed (45–50 °C (10⁻³ mm)) to give 107 mg (68%) of **5** (note: the benzoelassovalene was transferred in a glove bag filled with argon). Two additional sublimations gave an analytical sample, mp 76–77 °C; $\lambda_{max}^{isooctane}$ 264 nm (ε 44 000); $\delta_{TMS}^{CDCl_3}$ 7.56–7.16 (m, 4), 6.71 (br d, J = 2 Hz, 2), 6.43 (dd, J = 5.5 and 2 Hz, 2), 6.17 (dd, J = 5.5 and 2.5 Hz, 2), 4.10–3.88 (m, 1), and 2.57 (d with further splitting, J = 7 Hz, 1); ^{13}C NMR (CDCl₃) 145.73, 137.91, 136.29, 132.08, 130.62, 125.17, 117.94, 56.87, and 45.05 ppm; m/e 204.0942 (calcd 204.0939).

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.08; H, 6.03.

1,2-Benzo-Δ²,⁶-hexalin-9,10-dicarboxylic Anhydride (21).[19] A mixture of 125 g (0.625 mol) of 3,4-dihydro-1,2-naphthalic anhydride **(20)**[18] and 375 mL of 1,3-butadiene was heated at 100 °C in a 3-L autoclave for 96 h. The cooled autoclave was rinsed with ether and the washings were combined with the original contents. Low-boiling compounds were removed on a rotary evaporator and the residue was vacuum distilled (*caution:* near the end of the distillation the residue becomes very viscous and begins to smoke; all operations should cease at this point). The fraction having bp 160–170 °C (1 mm) solidified when stirred with a small amount of pentane. This solid was recrystallized from benzene–hexane to give **21**, mp 81–82 °C, in 53% yield; $\delta_{TMS}^{CDCl_3}$ 7.75–7.60 (m, 1), 7.33–7.05 (m, 3), 6.02 (m, 2), and 3.48–1.65 (m, 8).

cis-9,10-Bis(hydroxymethyl)-1,2-benzo-Δ²,⁶-hexalin (22a). To a slurry of 20.2 g (0.53 mol) of lithium aluminum hydride in 700 mL of tetrahydrofuran was added dropwise under nitrogen a solution of 84 g (0.33 mol) of **21** in 700 mL of the same solvent. After the addition was complete, the reaction mixture was heated at reflux for 22 h and cooled in an ice–water bath. Excess hydride was hydrolyzed with 125 mL of saturated sodium sulfate solution. The inorganic salts were removed by suction filtration and washed with tetrahydrofuran (2 × 500 mL). The combined filtrates were evaporated to give 77 g (95%) of **22a**, mp 108.5–109 °C (from benzene); $\nu_{max}^{CHCl_3}$ 3270 and 1060 cm⁻¹; $\delta_{max}^{CDCl_3}$ 7.23–7.07 (m, 4), 5.53 (m, 2), 4.11–3.75 (m, 4), 3.58 (br s, 2), 2.89 (t, J = 7 Hz, 2), 2.29 (br s, 3), and 1.95–1.59 (m, 3).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.36; H, 8.21.

cis-9,10-Bis(methanesulfonyloxymethyl)-1,2-benzo-Δ²,⁶-hexalin (22b). Reaction of 67 g (0.274 mol) of **22a** with 74.5 g (0.713 mol) of methanesulfonyl chloride in 400 mL of pyridine below −10 °C as described above gave 103 g (93%) of **22b**, mp 102.5 °C dec (from benzene–hexane); $\nu_{max}^{CHCl_3}$ 1360 and 1170 cm⁻¹; $\delta_{TMS}^{CDCl_3}$ 7.26–7.10 (m, 4), 5.62 (m, 2), 4.48 (s, 2), 4.29 (s, 2), 3.15–2.90 (m, 2), 2.99 (s, 3), 2.83 (s, 3), and 2.50–1.87 (m, 6).

Anal. Calcd for $C_{18}H_{24}O_6S_2$: C, 53.98; H, 6.04. Found: C, 53.89; H, 6.01.

2,3-Benzo-12-thia[4.4.3]propella-2,8-diene (23). Reaction of **22b** (16.0 g, 0.04 mol) with sodium sulfide nonahydrate (28.8 g, 0.12 mol) in anhydrous HMPA (250 mL) in the predescribed manner afforded after alumina chromatography (benzene elution) 8.2 g (85%) of **23**, mp 70–71 °C (from hexane); $\delta_{TMS}^{CDCl_3}$ 7.33–7.04 (m, 4), 5.51 (m, 2), 3.02

(s, 2), 3.07–1.73 (m with triplets at 2.94 and 2.87, 10); m/e 242.1133 (calcd 242.1129).

Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49. Found: C, 79.41; H, 7.56.

2,3-Benzo[4.4.2]propella-2,8,11-triene (24). A mixture of 30.5 g (0.126 mol) of **23**, 17.4 g (0.13 mol) of N-chlorosuccinimide, and 350 mL of carbon tetrachloride was heated at reflux under nitrogen for 3 h. The reaction mixture was cooled and the precipitated solid was removed by suction filtration. The filtrate was evaporated to leave a light yellow oil which was dissolved directly in 400 mL of chloroform. With cooling in a dry ice–carbon tetrachloride bath, there was added dropwise 336 mL (0.252 mol) of 0.75 M monoperphthalic acid in ether. After the addition was completed, the reaction mixture was stirred at room temperature overnight and the precipitated phthalic acid was removed by suction filtration. The filtrate was washed with 0.5 N sodium hydroxide solution (2 × 150 mL) and brine (2 × 150 mL), dried, and evaporated. Last traces of solvent were removed under high vacuum to give a mixture of α-chloro sulfones as a foamy, pale yellow solid, mp 65–110 °C; m/e 308.0642 (calcd 308.0638).

A solution of this epimeric mixture in 500 ml of anhydrous tetrahydrofuran was placed under nitrogen and cooled in a dry ice–carbon tetrachloride bath. Potassium $tert$-butoxide (79.7 g, 0.71 mol) was added in one portion and the mixture was then heated at reflux with stirring for 2.5 h, cooled, and diluted with water to approximately 5 L. The aqueous solution was continuously extracted with 500 mL of ether. Removal of the ether gave a dark-colored oil which was purified by chromatography on alumina (pentane elution). There was isolated 13.6 g (51.7% from **23**) of **24**, mp 35–36 °C (from pentane); ν_{max}^{neal} 3001 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.31–7.06 (m, 4), 5.84 (pseudo t, 3), 5.64 (d, J = 3 Hz, 1), 2.84–2.54 (m, 3), 2.29 (m, 1). 2.01 (m, 2), and 1.86–1.17 (m, 2); m/e 208.1254 (calcd 208.1252).

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.91; H, 7.82.

2,3-Benzo[4.4.2]propella-2,7,9,11-tetraene (25). A mixture of 13.0 g (62.4 mmol) of **24**, 21.0 g (65.5 mol) of pyridinium hydrobromide perbromide, 225 mL of glacial acetic acid, and 225 mL of carbon tetrachloride was stirred at room temperature for 3 h. The solution was diluted with 450 mL of water and the layers were separated. The aqueous phase was extracted with carbon tetrachloride (2 × 150 mL) and the combined organic layers were washed with water (2 × 150 mL), 0.5 N sodium hydroxide solution (2 × 150 mL), and again water (2 × 150 mL), prior to drying and evaporation. The dibromide mixture so obtained was a white solid, mp 89–101 °C; $\delta_{TMS}^{CDCl_3}$ 7.15 (m, 8), 6.44 (d, J = 3 Hz, 1), 6.23 (d, J = 3 Hz, 1), 5.98 (d, J = 3 Hz, 1), 5.76 (d, J = 3 Hz, 1), 5.02–4.42 (m, 4), 3.16–3.06 (m, 1), 2.92–2.28 (m, 10), and 2.13–1.13 (m, 5); m/e 365.9624 (calcd 365.9620).

This solid was dissolved in anhydrous HMPA (600 mL) and blanketed with nitrogen. There were then added in one portion 26.5 g (0.624 mol) of dry lithium chloride and 46.1 g (0.624 mol) of dry lithium carbonate, and the resulting mixture was stirred at 85–90 °C for 24 h, cooled, and diluted with 2.4 L of water. The solution was extracted with pentane (4 × 500 mL) and the combined extracts were washed with water (4 × 400 mL), dried, and evaporated to leave a dark-colored oil. Chromatography on alumina (benzene elution) gave 8.0 g (62% from **24**) of **25**, mp 43.5–44 °C (from pentane); ν_{max}^{neal} 3003 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.33–7.04 (m, 4), 6.34–5.52 (m, 6), 2.78–2.56 (m, 2), and 2.01–1.22 (m, 2); m/e 206.1088 (calcd 206.1095).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H. 6.84. Found: C, 92.80; H, 6.84.

Diels–Alder Reaction of 25 with N-Methyltriazolinedione. To a solution of 7.0 g (34 mmol) of **25** in 250 mL of pentane-ethyl acetate (4:1) cooled in a dry ice–isopropyl alcohol bath was added dropwise with stirring a solution of 3.8 g (34 mmol) of N-methyltriazolinedione in 50 mL of ethyl acetate. The resulting mixture was allowed to warm to room temperature and the precipitated adduct was collected by suction filtration and dried, 9.8 g (90.5%). Analytically pure **26** was obtained by recrystallization from benzene-cyclohexane, mp 193–193.5 °C; $\nu_{max}^{CHCl_3}$ 1765 and 1700 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.60–7.17 (m, 4), 6.28 (pseudo t, 2), 5.99 (d, J = 3 Hz, 1), 5.73 (d, J = 3 Hz, 1), 5.49 (m, 1), 4.70 (m, 1), 2.95–2.67 (m with sharp s at 2.90, 5), and 2.01 (pseudo t, 2); m/e 319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.19; H, 5.51; N, 12.85.

Photoisomerization of 7,8-Dihydro-N-methyl-1,4:4a,8a-diethenobenzo[f]phthalazine-2,3(1H,4H)-dicarboximide (26). A solution of 1.00 g (3.13 mmol) of **26** in 400 mL of benzene-acetone (1:1) was

irradiated for 1 h using a 450-W Hanovia lamp through Corex (80% completion; further irradiation resulted in formation of excess amounts of solvent photoproducts). The reaction mixtures from three such runs were combined, evaporated, and chromatographed on silica gel (9:1 ether-hexane elution) to give 781 mg (25% based on consumed **26**) of **28**. Elution with ether gave 849 mg of unreacted **26**. Continued elution with 1:1 ether-chloroform gave 2.24 g (71% based on consumed **26**) of cubyl derivative **27**.

Pure **28** was obtained by recrystallization from benzene-cyclohexane, mp 147–147.5 °C; $\nu_{max}^{CHCl_3}$ 1770 and 1720 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.28–7.07 (m, 3), 5.96 (m, 2), 5.44 (d, J = 3.5 Hz, 1), 4.85 (d, J = 3.5 Hz, 1), 3.37 (m, 2), 2.92 (s, 3), 2.85–2.71 (m, 2), and 2.45–2.22 (m, 2); ^{13}C NMR (CDCl$_3$) 158.11, 157.80, 139.59, 138.75, 135.31, 130.91, 130.68, 128.09, 127.70, 127.61, 127.03, 121.35, 58.90, 53.46, 41.60, 41.54, 27.75, 25.40, 25.34 ppm; m/e 319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}h_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.09; H, 5.36; N, 12.79.

Pure **27** was obtained by recrystallization from benzene-cyclohexane, mp 148–150 °C; $\nu_{max}^{CHCl_3}$ 1775 and 1715 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.30–7.11 (m, 4), 5.40 (m, 1), 4.77 (m, 1), 3.63 (m, 2), 310–2.98 (m, 2), 4.77 (m, 1), 3.63 (m, 2), 310–2.98 (m, 2), 3.02 (s, 3), 2.85–2.64 (m, 2), and 2.14–1.55 (m, 2); m/e 319–1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.22; H, 5.49; N, 12.76.

Ag$^+$-Catalyzed Rearrangement of 27. A solution of 500 mg (1.57 mmol) of **27** and 7.98 g (47.0 mmol) of silver nitrate in 60 mL of tetrahydrofuran-water (4:1) was heated in a sealed tube at 120 °C for 18 h. The solution was cooled, filtered through Celite, and concentrated. The residue was extracted with chloroform (3 × 20 mL) and the combined extracts were washed with water (2 × 10 mL) and brine (2 × 10 mL), prior to drying and evaporation. There was obtained 420 mg (84%) of **29**, mp 209 °C (from benzene-cyclohexane); $\nu_{max}^{CHCl_3}$ 1760 and 1700 cm^{-1}; $\nu_{TMS}^{CDCl_3}$ 7.64–6.93 (m, 4), 5.69 (m, 1), 5.00 (m, 1), 3.00 (s, 3), and 2.69–1.70 (m, 8); m/e 319.1324 (calcd 319.1320).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.51; H, 5.40; N, 12.89.

Oxidative Dehydrogenation of 29. A mixture of 200 mg (0.63 mmol) of **29**, 116 mg (0.65 mmol) of N-bromosuccinimide, 1 mg of azobisisobutyronitrile, and 25 mL of carbon tetrachloride was irradiated with a tungsten DYV projector lamp for 1 h. The solution was filtered and evaporated to leave a foam which was taken up in chloroform (75 mL) and washed with saturated sodium bicarbonate solution and brine prior to drying. Solvent removal left a rather unstable solid which was utilized without added purification; $\delta_{TMS}^{CDCl_3}$ 7.75–6.97 (m, 4), 5.62 (m, 1), 5.42 (m, 1), 4.93 (m, 1), 3.20 (d, 1), 3.00 (s, 3), and 3.00–1.95 (m, 5).

A solution of benzylic bromide in 50 mL of tetrahydrofuran under nitrogen was treated with 0.48 g (1.56 mmol) of DBU and stirring at room temperature was maintained overnight. The solvent was evaporated and the residue was dissolved in chloroform (20 ml). The solution was washed with 3% hydrochloric acid (2 × 10 mL), 10% sodium bicarbonate solution (2 × 10 mL), and water (10 mL), prior to drying and evaporation. The dark-colored residue was chromatographed on Florisil (chloroform elution) to give mg (80%) of **30**, mp 181–183 °C; $\delta_{TMS}^{CDCl_3}$ 7.73–6.97 (m, 4), 6.20 (m, 2), 5.63 (m, 1), 5.10 (m, 1), 2.88 (s, 3), 2.50–1.95 (m, 3), and 0.95 (d, 1); m/e 317.1169 (calcd 317.1164).

Hydrolysis–Oxidation of 30. (All solvents were purged with argon prior to use and all solutions were maintained under an argon atmosphere.) a mixture of 317 mg (1.36 mmol) of **30**, 40 mg (13.6 mmol) of sodium hydroxide, and 30 mL of isopropyl alcohol was mechanically stirred and heated at reflux for 1 h. The resulting solution was cooled to 0 °C, acidified to pH 5–6 with 50% acetic acid, then basified with 50% aqueous ammonium hydroxide to pH 9 and diluted with pentane (50 ml). To the clear yellow solution was added 87 mg (13.6 mmol) of activated manganese dioxide.[47] Immediate gas evolution was noted. After 2 h, the suspension was filtered through Celite and the filtrate rapidly extracted with pentane (3 × 15 mL). The combined pentane layers were dried and evaporated under high vacuum below − 30 °C. The resulting off-white solid could not be transferred without decomposition. Direct sublimation into the MS-9 mass spectrometer gave a molecular ion peak for **3** at m/e 204.0944 (calcd 204.0939).
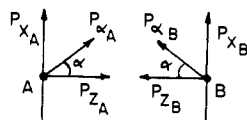
Figure 5.

12115). Thanks are also due to Dr. Richard Burson for his expert assistance in the attempted isolation of **3**, and to Professors William Kern and Kenneth Lipkowitz for helpful discussions.

Appendix

The Mulliken formulas are modified for the symmetric geometry shown in Figure 5, where the vectors P_{x_i}, P_{z_i}, P_{α_i} are the axial directions of p orbitals of atom i. We wish to evaluate the overlap integral $\langle p_{\alpha A} | p_{\alpha B} \rangle$. The p_{α_i} are simply linear combinations of the orthogonal basis orbitals p_{x_i} and p_{z_i}.

$$p_{\alpha_i} = p_{z_i} \cos \alpha + p_{x_i} \sin \alpha$$

so

$$\langle p_{\alpha A} | p_{\alpha B} \rangle = \langle p_{z_A} \cos \alpha + p_{x_A} \sin \alpha | p_{z_B} \cos \alpha + p_{x_B} \sin \alpha \rangle$$

Since $\langle p_{z_A} | p_{x_B} \rangle \equiv 0$ by symmetry, then

$$\langle p_{\alpha A} | p_{\alpha B} \rangle = \cos^2 \alpha \langle p_{z_A} | p_{z_B} \rangle + \sin^2 \alpha \langle p_{x_A} | p_{x_B} \rangle$$

Integrals of the form $\langle s_A | p_{\alpha B} \rangle$ are evaluated similarly:

$$\langle s_A | p_{\alpha B} \rangle = \langle s_A | p_{z_B} \cos \alpha + p_{x_B} \sin \alpha \rangle$$

Again $\langle s_A | p_{x_B} \rangle \equiv 0$ by symmetry and $\langle s_A | p_{\alpha B} \rangle = \cos \alpha \langle s_A | p_{z_B} \rangle$. The integrals $\langle s_A | p_{z_B} \rangle$, $\langle p_{x_A} | p_{x_B} \rangle$ and $\langle p_{z_A} | p_{z_B} \rangle$ have the analytic, parameterized solutions given by Mulliken.

Supplementary Material Available: Table VII (final fractional coordinates for benzoelassovalene) and Table VIII (observed and calculated structure factors for benzoelassovalene) (9 pp). Ordering information is given on any current masthead page.

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$$\vec{\eta} = (BA) \times (BC)/\{|BA||BC| \sin(\angle ABC)\}.$$

The three components of $\vec{\eta}$ are the direction cosines of the normal relative to the orthogonal axes of the coordinate system. Many standard cystallographic geometry programs yield such direction cosines as output from a least-squares plane calculation. The angle α can be found from

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