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Synthesis and Electronic Properties of 2a,8b-Dihydrocyclopent[*cd*]azulenes (Elassovalenes)

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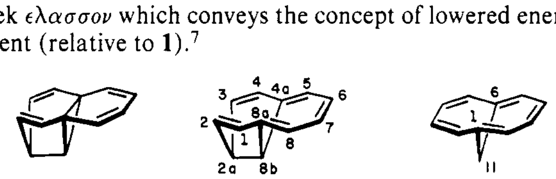
Abstract: The synthesis of 2a,8b-dihydrocyclopent[*cd*]azulene (elassovalene), its $Cr(CO)_3$ complex, and two methoxy derivatives, the determination of their ^1H, ^{13}C, UV, and PE spectra, and measurements of diamagnetic susceptibility are described. A common starting material for the entire range of compounds was urazole **5**. In a most efficient route, bromination–dehydrobromination of **5** provided the corresponding norcaradiene, oxidative hydrolysis of which gave elassovalene (**2**) directly. An alternative approach began with ozonolysis of **5**, conversion to dimesylate **7**, and treatment of the latter with strong base. A variety of oxygenated substituents could be placed upon the cyclohexene ring of **5**, sometimes with high levels of stereochemical control, depending upon the particular oxidative technique employed. Further functional group manipulation ultimately led to isolation of the air-sensitive 5- and 6-methoxyelassovalenes. The combined weight of spectral evidence reveals these molecules to possess at a minimum some degree of homoaromatic character in the bridged cycloheptatriene portion of their structure. This level of interaction is consistent in particular with ^1H NMR, PE, and diamagnetic exaltation criteria observed in particular for the parent hydrocarbon. These results, in contrast, do not provide reliable information on the level of transannular interaction, if any, at the "open" end of these molecules.

Interest in our laboratory has recently been focused on several facets of higher order homoaromaticity[3] and the possible realization of neutral homoaromatic character.[4,5] Consequently, when methodology for varied 2,8-annulation of semibullvalene, the system most closely approaching the realization of homoaromatic six-electron cyclic delocalization ($\Delta G^{\ddagger}$ = 5.5 kcal/mol at −143 °C),[6] became available,[4] we were led to examine the effect of bridging this hydrocarbon at C_2 and C_8 with a 1,3-butadienyl moiety. The resultant molecule (**1**) was expected to be unstable relative to the pentaene form **2** to which it is related by a simple [3,3]-sigmatropic shift. Were a ring current to operate in **2**, a mesovalent Hückel-like molecule would be in hand and neutral homoaromaticity would be realized experimentally for the first time. For convenience, we have named this hydrocarbon "ellasovalene" from the Greek ελασσον which conveys the concept of lowered energy content (relative to **1**).[7]



1 **2** **3**

Although the magnitude of homoaromatic stabilization which can be anticipated for uncharged molecules must be appreciably diminished relative to charged entities due to the lack of a driving force for charge delocalization, the structural similarity of bishomo[10]annulene **2** to **3**[8] and higher bridged annulenes[9] suggested that 2,3 overlap might gain significance. The existence in **3** of *non*-negligible 1,6 interaction as sug-

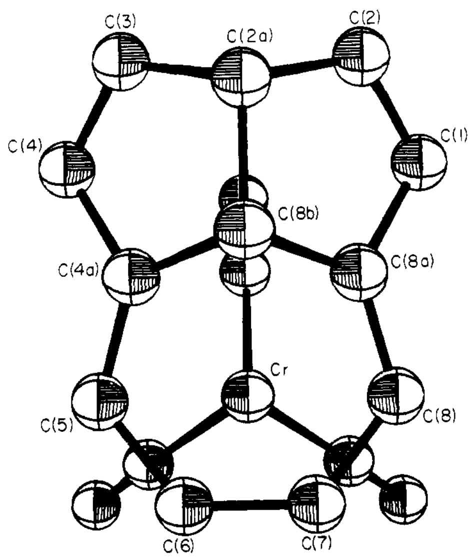
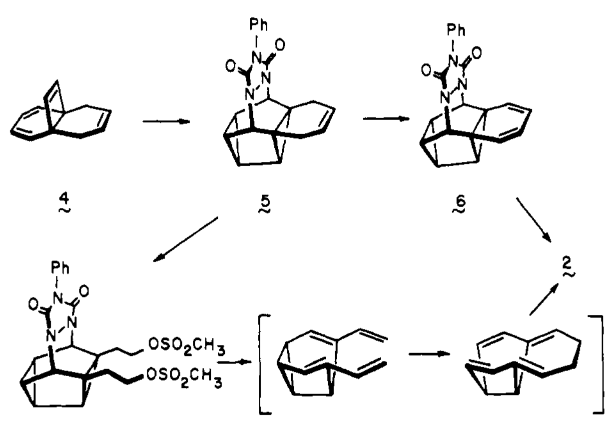


Figure 1. Final x-ray model for complex **12** less hydrogens. A molecular mirror plane contains atoms C_{2a}, C_{8b}, Cr, and one CO.

gested by theory[10] appears to be manifested in its photoelectron ($\beta_{1,6} = -2.0$ eV),[11] ultraviolet,[12] and ^{13}C NMR spectra.[13] X-ray crystal structure analysis of its 11,11-dimethyl,[14] 11,11-difluoro,[15] and 2-carboxylic acid derivatives[16] reveal the C_1–C_6 distances to be 1.780, 2.25; and 2.257 Å, respectively, showing the structures of these compounds to be quite susceptible to substituent perturbations. Accordingly, it still remains unclear exactly to what extent the properties of **3** are modified by homoaromatic interaction superimposed upon the peripheral 10π electron delocalization.

The properties of **2** are therefore of particular interest. The observable consequences of homoaromatic stabilization cannot be expected to be as pronounced as those of more classical aromaticity; nevertheless, our current state of knowledge makes available a number of tools which can be brought to bear on this general question. We now describe the synthesis of elassovalene and its 5- and 6-methoxyl derivatives together with an experimentally based appraisal of their electronic character.

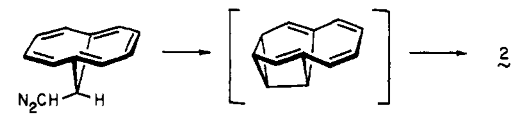
Synthetic Approaches to Elassovalene. Our initial preparation of **2**[4a] began with the elaboration of [4.4.1]propella-2,4,8,11-tetraene (**4**),[4e] its three-step conversion to **5**,[4e] and



bromination–dehydrobromination of this diazasnoutane.[4g] Alkaline hydrolysis of **6** was followed by mild air oxidation of the saponification product. The resulting diazo compound decomposed rapidly in situ via a retro-homo Diels–Alder process with clean formation of elassovalene (**2**). This hydrocarbon, which proved to be an air-sensitive pale yellow liquid at room temperature, could be obtained as fine needles (mp 7-8 °C) when recrystallized from methanol.

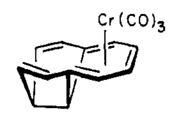
Alternatively, **5** could be readily transformed into dimesylate **7**.[4i] With potassium *tert*-butoxide in dimethyl sulfoxide containing a trace of water, this diazasnoutane was converted by concomitant hydrolysis[17] and dual elimination of methanesulfonic acid into an intermediate, oxidation of which with air or copper(II) led directly to **2**. The expectation that **8** (only one semibullvalene form shown) would be capable of symmetry-allowed bond reorganization to deliver **9** was evidently borne out, although the susceptibility of **9** to mild oxidation was more marked than anticipated.[18]

Complementary to our approaches is that devised by Vogel wherein diazo compound **10** was generated and allowed to decompose.[19] Under these conditions, elassovalene was formed in 5-7% yield (by way of **11**) together with several other products.



10 **11** **2**

(Tricarbonyl)elassovalenechromium. Whereas elassovalene proved in our hands to be unreactive toward $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Mo(CO)_6$, $Mo(CO)_3(THF)_3$, and $Cr(CO)_6$, heating with $Cr(CO)_3(NH_3)_3$[20] in hexane for 50 h successfully afforded a dark red crystalline complex of composition $C_{12}H_{10}{\cdot}Cr(CO)_3$ (*m/e* 290.0030). This substance was obtained in analytically pure form by sublimation and subsequent recrystallization from chloroform–hexane (36% yield). Because the chromium atom has retained three CO groups, six electrons in the hydrocarbon must be involved in bonding to the metal. The observation that **2** is regenerated upon treatment of **12** with diethylenetriamine[21] discounts the possibility



12

of structural rearrangement. Insight into the π-electronic nature of the complex as provided by its IR, UV, and 100-MHz ^{1}H NMR spectra (see Experimental Section) determined **12** to possess a cycloheptatriene–$Cr(CO)_3$ part structure. The question of the stereochemical orientation of the metallic center relative to apical carbons C_{2a} and C_{8b} was resolved in favor of **12** by three-dimensional x-ray crystal structure analysis.

The complex crystallizes with four molecules in an orthorhombic unit cell of dimensions $a = 11.63$ (2), $b = 9.45$ (1), and $c = 11.59$ (2) Å. The systematic extinctions for $h0l$ (absent if $h = 2n + 1$) and $0kl$ (absent if $k + l = 2n + 1$) could arise from the space groups P_{na2_1} ($C_{2v}{}^9$) or P_{nam} ($D_{2h}{}^{16}$, alternate setting). The latter space group would require a molecular mirror plane. All unique reflections with $\sigma \leq 25°$ were measured using an automated Hilger-Watts diffractometer and Nb-filtered Mo Kα x-rays (0.7107 Å). A total of 856 of the 1180 reflections measured had $F_o{}^2 \geq 3\sigma(F_o{}^2)$ after correction for Lorentz and polarization effects; these were considered observed and used in all subsequent calculations. The structure was phased by the heavy atom method, and space group P_{nam} with its required molecular mirror plane was strongly indicated. Full-matrix least-squares refinements with anisotropic thermal parameters for Cr, C, and O and isotropic thermal parameters for H rapidly converged to a discrepancy index of 0.044.[22] Figure 1 is a computer-generated drawing of the final x-ray model less hydrogens.[23] Estimated standard deviations in bond lengths are 0.007 Å and in bond angles 0.5°.[24]

There is no evidence for substantive bonding between the atom pair C_2-C_3 (2.543 (9) Å). The five-membered rings are planar with no deviations greater than 0.02 Å from the best least-squares plane. The seven-membered ring is in an envelope conformation with atoms C_{8a}, C_8, C_7, C_6, C_5, and C_{4a} essentially planar (maximum deviation from best plane is 0.11 Å) while C_{8b} is 0.86 Å displaced from this plane. The double bonds in the five-membered rings are of normal length (1.336 Å) while those in the seven-membered ring are lengthened (average 1.39 Å) presumably by donation to Cr. All C-H distances are between 0.95 and 1.00 Å. The remaining structural parameters appear in Table I.

The tricarbonylchromium group in **12** is seen to adopt that orientation relative to the triene ligand (cf. **A**) which has pre-

A B

viously been observed for tricarbonyl-*exo*-7-phenylcycloheptatriene[25] and hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium[26] rather than that assumed by tricarbonyl-1,6-methano[10]annulenechromium,[27] tricarbonyltricyclo[4.3.1.0^{1,6}]deca-2,4-dienechromium,[28] and tricarcarbonylbicyclo[4.4.1]undeca-1,3,5-trienechromium,[29] where the carbonyl groups are rotated by 60° (cf. **B**). In the latter group of molecules, the distances separating the bridgehead carbon atoms were determined to be 2.14, 1.65, and 1.72 Å, respectively. The corresponding value for **12** (2.404 Å) differs in being a substantially wider gap. Whether this structural feature is also a property intrinsic to the free ligand cannot be ascertained from these data, since the effects of the crystallographic orientations **A** and **B** upon molecular structure have yet to be established. Therefore, the possibility that arrangement A may be more conducive to lengthening of the C_{4a}-C_{8a} distance cannot be summarily dismissed at this time.

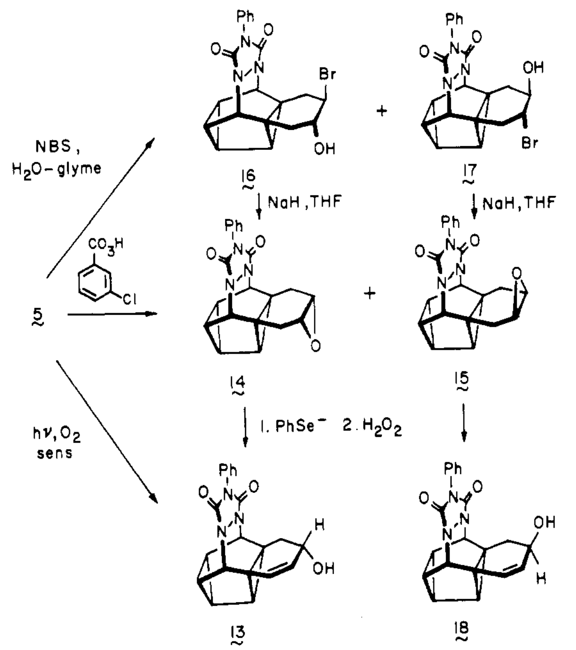
6-Methoxyelassovalene. Submission of **5** to the action of singlet ($^1\Delta_g$) oxygen (as generated by rose bengal photosensitization), followed by reduction of the resulting allylic hydroperoxide with sodium borohydride, proceeded with formation of a single alcohol (**13**) in 95% isolated yield after silica gel chromatography. To establish the configuration of this product, **5** was also subjected to peracid epoxidation. The major product (84%), isolated by direct crystallization, was formulated as anti stereoisomer **15** on the basis of its ^{1}H NMR spectrum which showed all four cyclopropyl protons to resonate in the δ 2.30-1.70 region. For less dominant epoxide **14** (7%), the presence of three comparable cyclopropyl protons was clearly displayed (δ 2.25-1.85); however, the fourth appeared as a doublet centered at δ 1.36, the upfield shifting arising because of diamagnetic shielding by the proximate oxygen atom.[30,31] For the purpose of obtaining larger quantities of **14**, **5** was treated with *N*-bromosuccinimide in aqueous glyme.[32] The two bromohydrins **16** (70%) and **17** (15%) so produced were individually converted to **14** and **15** with sodium hydride in refluxing tetrahydrofuran.

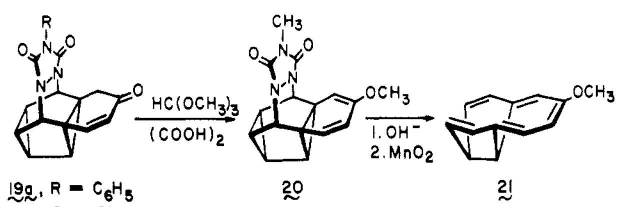
Treatment of **14** with basic alumina,[33] or preferably with phenylselenide anion followed by hydrogen peroxide,[34] afforded allylic alcohol **13** fully identical with the photooxygenation product. Epoxide **15** was similarly converted to anti alcohol **18.** We see therefore that electrophilic attack on **5** by peracid and bromonium ion proceeds preferentially from the sterically less demanding anti direction. Yet, its photosensitized oxygenation yields exclusively the syn alcohol as the result of $^1O_2$ quenching by the hydrazide functionality which is positioned on the anti structural surface.[35,36]

Although **13** was easily oxidized to enone **19a** with manganese dioxide, consistent results were obtained only when the reagent was prepared by the Attenburrow method.[37] Under the most favorable conditions, **18** invariably reacted more slowly and afforded lower yields of the same ketone, as expected. Conversion of the *N*-methyl congener of **13** to **19b** proceeded readily in the presence of Collins' reagent.[38] Noteworthy features of the ^{1}H NMR spectrum of **19a** include a pair of downfield doublets (J = 10 Hz) at δ 7.10 and 6.74 due to the olefinic protons, a multiplet at 5.01 for the nonequivalent bridgehead (>CHN<) hydrogens, an AB pattern at 2.93 and 2.80 (J_{AB} = 18 Hz) assignable to the methylene group, and a broad multiplet of area 4 at 2.35-1.80 for the cyclopropyl protons.

Table I. Pertinent Bond Distances and Bond Angles in Complex **12**

Bond	Distance, Å	Angle	Deg
C_1-C_2	1.336	C_1-C_2-C_{2a}	112.3
C_1-C_{8a}	1.456	C_1-C_{8a}-C_8	129.6
		C_1-C_{8a}-C_{8b}	107.8
C_2-C_{2a}	1.511	C_2-C_1-C_{8a}	111.2
C_{2a}-C_{8b}	1.560	C_2-C_{2a}-C_3	114.7
C_6-C_7	1.39	C_2-C_{2a}-C_{8b}	103.2
C_7-C_8	1.434	C_{2a}-C_{8b}-C_{8a}	105.3
C_8-C_{8a}	1.388	C_{4a}-C_{8b}-C_{8a}	106.2
C_{8a}-C_{8b}	1.503	C_6-C_7-C_8	128.0
		C_7-C_8-C_{8a}	124.5
		C_8-C_{8a}-C_{8b}	122.1

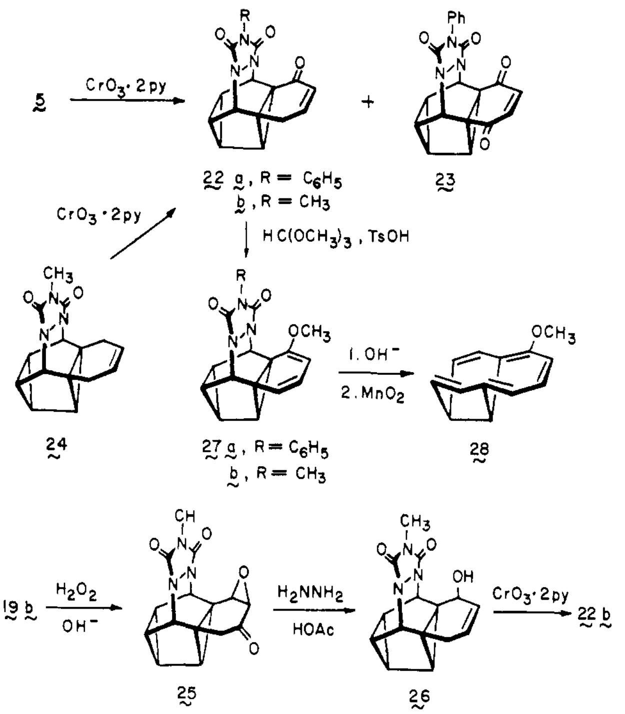




The more readily soluble enone **19b** underwent smooth conversion to methoxydiene **20** when exposed to a large excess of trimethyl orthoformate. This reaction, catalyzed best by oxalic acid, proved to be quite sensitive and gave other unidentified products when lesser amounts of the orthoester were used.[39] Interesting emergent ^{1}H NMR patterns for **20** include a vinyl region composed of a doublet (J = 9.5 Hz) at δ 6.20, doublet of doublets (J = 9.5 and 2.0 Hz) at 5.70, and a second doublet (J = 2.0 Hz) at 5.05; the cyclopropyl protons appear at δ 2.37 (m, 1), 2.00 (m, 2), and 0.63 (d, J = 3.5 Hz, 1). The last signal, due to the hydrogen positioned below the diene unit, is located only 0.06 ppm downfield from its location in the unsubstituted diene.

Hydrolysis-oxidation of **20** gave rise to the desired 6-methoxyelassovalene (**21**), a yellow, air-sensitive, low-melting solid, whose spectral properties serve to characterize the material unequivocally (vide infra).

5-Methoxyelassovalene. Two approaches were utilized to gain access to **28**. In the first, **5** was oxidized with Collins' re-



agent and converted under these conditions[40] to α,β-unsaturated ketone **22a** and enedione **23** in moderate yields. The monoketone exhibits ^{1}H NMR absorptions (in $CDCl_3$) at δ 6.59 (d of t, 1H), 5.97 (d of t, 1H), and 2.87 (d of d, 2H), fully compatible with the assigned structure (compare **19a**). In characteristic fashion, **23** is seen to possess equivalent olefinic protons (δ 6.62, s). When this reaction was applied to **24, 22b** was isolated in 43% yield.

Conclusive evidence that oxidation of **24** did not involve migration of the double bond was obtained by epoxidation of **19b** with alkaline hydrogen peroxide in methanol,[41] treatment of **25** with hydrazine hydrate and acetic acid in refluxing dioxane,[42] and Collins oxidation of allylic alcohol **26**. The well-established 1,3 transposition characteristics of the Wharton procedure require that **22b** be the ketone in which the carbonyl group is flanked by a cyclopropane ring and double bond. Interestingly, neither **22a** nor **22b** has given any indication of the presence of the dienol (norcaradiene) form in detectable quantities.

Although the stereochemistry of **25** was not rigorously proven, the anti epoxide was anticipated from steric considerations and is supported by spectral data. Perhaps most telling is the finding that the four cyclopropyl protons in **25** appear as a closely spaced multiplet at δ 2.20–2.00. Were the epoxide ring oriented syn to the cyclopropyl moieties, the proximate proton would be expected to be markedly shielded (see above), but it is not.

The direct oxidation of **5** or **24** is decidedly the method of choice for preparing **22a** and **22b.** The ability of selenium dioxide in dimethoxyethane to achieve the same end result was briefly examined. Somewhat surprisingly, this reagent gave neither the desired allylic alcohol nor α,β-unsaturated ketone, but afforded instead the corresponding diene.

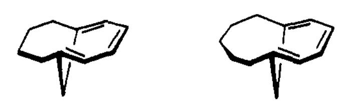
Enones **22a** and **22b** were smoothly transformed to the methoxynorcaradienes **27a** and **27b** with excess trimethyl orthoformate containing a catalytic quantity of *p*-toluenesulfonic acid. Hydrolysis-oxidation of either urazole led easily to **28;** the use of **27b** was preferred since product contamination by aniline was then not a problem. Like **21,** this elassovalene proved to be a yellow, air- and acid-sensitive solid, crystals of which were unfortunately unsuitable for x-ray crystal structure determination.

Electronic Spectra. The ultraviolet spectrum of **2** as recorded in isooctane solution is characterized by a pair of maxima at 249 (ϵ 31 000) and 335 nm (ϵ 2800). Since 2,8-annulated semibullvalenes typically exhibit relatively weak absorption on the fringe of intense and absorption, this property of **2** expectedly does not correspond to that of such fluxional molecules. Rather, the electronic nature of elassovalene accords to a great extent with those of bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene [**29,** $\lambda_{max}^{cyclohexane}$ 248 (ϵ 39 800) and 327 nm (3730)][43] and 1,6-divinylcycloheptatriene [**30,**

29 30

$\lambda_{max}^{cyclohexane}$ 237 (ϵ 45 200), 245 (57 500), and 300 nm (6300)],[19] and rather well with that of 1,6-methano[10]annulene [**3,** $\lambda_{max}^{cyclohexane}$ 256 (ϵ 68 000), 259 (63 000), and 298 nm (6200)].[44,45] The annulene should not be expected to manifest fully comparable spectral properties, because the delocalization which is possible in this π frame is interrupted completely in **30** and by a second methano bridge in **2** and **29.**

Comparison of these data with those previously recorded in cyclohexane for the 1,6-annulated cycloheptatrienes **31** [λ_{max} 257 nm (ϵ 5140)][46] and **32** [λ_{max} 272 nm (ϵ 4600)][46]



31 32

discloses that the extended conjugation present in **2, 29,** and **30** is indeed reflected in their ultraviolet spectra. Furthermore, the π-electron overlap in the rather conformationally flexible **30** appears to be rather similar to that in the more constrained molecules. However, this parallelism should not be construed as indicative of peripheral delocalization or the lack thereof.

The electronic spectrum of 6-methoxyelassovalene [**21,** $\lambda_{max}^{isooctane}$ 247 (ϵ 54 000) and 327 nm (4000)] corresponds closely to that of **2.** Interestingly, positioning of the methoxyl group at C_5 as in **28** results in the appearance of three maxima [$\lambda_{max}^{isooctane}$ 238 (ϵ 29 000), 262 (37 000), 348 nm (1800)], the last of which is bathochromically shifted to an appreciable extent relative to the long-wavelength bands in **2, 29,** and even **3.**

^{1}H and ^{13}C NMR Spectra. Analysis of the ^{1}H NMR spectrum of elassovalene proved to be relatively straightforward. Specifically, the peripheral olefinic protons appear as three groups of multiplets in the region δ 6–7 (Figure 2). Because H_1–H_4 are insulated from H_5–H_8 (see **2** for numbering), all relevant coupling constants could be successfully determined by standard double resonance measurements. The key findings of this study include assignment of chemical shift to the AA'BB' cycloheptatriene part structure (δ 6.45–6.72, see Table II) and determination of the magnitudes of $J_{5,6}$ (= $J_{7,8}$) and $J_{6,7}$ as 6.5 and 11.0 Hz, respectively (Table III). This triene unit is therefore seen to be downfield shifted by approximately 1 ppm relative to **31** and **32,**[46] upfield shifted relative to **3,**[45] and at approximately the identical position observed for **29** and **30.**[19] The alternation in the vicinal coupling constants (ΔJ =

Table II. Summary of ^{1}H NMR Chemical Shift Data ($CDCl_3$, 100 MHz, 40 °C)

Proton	Chemical shifts, δ 2	21	28
1	6.45	6.43	6.25
2	6.02	5.93	6.43
2a	3.77	3.90	3.75
3	6.02	6.11	6.10
4	6.45	6.39	6.50–6.90
5	6.45	6.24	
6	6.72		5.83
7	6.72	6.04	6.50–6.90
8	6.45	6.30	6.50–6.90
8b	1.78	2.03	1.85

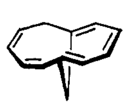
Table III. Summary of ^{1}H NMR Coupling Constant Data ($CDCl_3$, 100 MHz, 40 °C)

J, Hz	2	21	28
1,2 and/or 3,4	5.3	5.2	5.5
2,2a and/or 2a,3	2.4	2.7	2.0
2a, 8b	7.4	7.5	7.5
5,6 and/or 7,8	6.5	6.5	
5,7		1.5	
5,8		1.5	
6,7	11.0		

4.5), although less than in cycloheptatriene (ΔJ = 5.46), is rather appreciable and certainly much greater than that determined for **3** (ΔJ = 0.22).[47] If the trend toward equalization of these J values does indeed correlate with increased π-electron delocalization,[48] then our observations are consistent with the anticipated conclusion that methano[10]annulene enjoys greater "aromaticity" than elassovalene. However, no conclusions concerning the degree of homoaromatic stabilization in **2** can be reliably derived from these data. What is clear is the close parallelism between the downfield regions of all three elassovalenes.

In these compounds, the apical hydrogens H_{8b} and H_{2a} are positioned below the shielding cone of the cycloheptatriene moiety and beyond the "rim" of the carbocyclic frame, respectively. Accordingly, their signals are widely separated. In the case of **2**, these protons resonate at δ 1.78 and 3.77. The presence of a 5-methoxyl substituent exerts a minimal effect on either chemical shift (δ 1.85 and 3.75). By way of comparison, the 6-methoxyl group in **21** substantially deshields both protons (δ 2.03 and 3.90), a change which is accentuated still more upon η^6-coordination of the parent hydrocarbon to a $Cr(CO)_3$ unit as in **12** (δ 2.16 and 4.26). Since perturbation of the prevailing steric effects is not likely an issue in these examples, H_{8b} is seen to be a sensitive probe of the electronic features which prevail in the "closed" end of the elassovalenes.

A reasonable body of ^{1}H NMR information has been amassed to this time on 1,6-bridged cycloheptatrienes. As above, the syn oriented bridge proton lies beneath the π electron cloud and is subject to pronounced electronic shielding. But progression through a series as regular as **31** (δ 0.77), **32** (1.59), **29** (0.2), **33** (1.2),[43] **34** (0.04),[49] **35a** (0.63),[50] and **35b**



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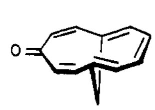

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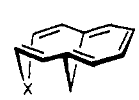


35 a, X = O
b, X = S

(0.21)[50] does not provide evidence of gradual alteration in the chemical shift of H syn (δ values given) with the size of the bracket, the degree and locus of unsaturation therein, or the presence of different heteroatoms. The consequence of this comparison is removal of any reasonable possibility that a basis for correlating greater or lesser degrees of cyclic delocalization might be founded reliably upon the spectral properties of a wide collection of such compounds. Such an analysis might have merit when very closely related molecules having identical frames, degrees of unsaturation, etc., are being compared, but this restriction severely limits the value of the method.

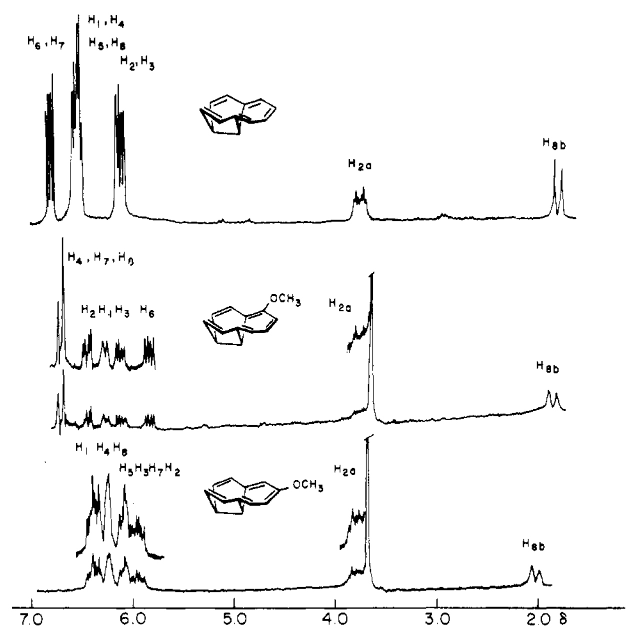


Figure 2. The 100-MHz NMR spectra of **2**, **21**, and **28** in $CDCl_3$ solution at 500-Hz sweep width.

At the present time, it is generally agreed that ^{13}C resonance frequencies are most affected by paramagnetic contributions[51] and stereochemical factors such as conformation and ring strain.[52] These considerations denote that a ring current will little influence shielding constants[53] and thereby relegate ^{13}C NMR spectroscopy to a less important role in assaying aromaticity and homoaromaticity. In actuality, the observation of ring-current effects by ^{13}C NMR is complicated by the fact that the peripheral carbons are neither strongly shielded nor strongly deshielded by electron delocalization because they lie directly between the shielding and deshielding regions.[54] It becomes necessary then to observe carbon atoms inside and outside of the current loop. In this context, the observations of DuVernet and Boekelheide on dihydropyrene systems[55] and of Trost and Herdle on pyracyclene derivatives[56] constitute the most convincing evidence presently available that ^{13}C chemical shifts are influenced to some extent by diatropism and paratropism, respectively.

On this basis, the CMR shifts of the apical carbon atoms 2a and 8b in **2, 21** and **28** should comprise the best probes of homoaromatic delocalization in these elassovalenes. The spectral data for these compounds as established by single frequency off-resonance decoupling studies are compiled in Table IV.[57] The only appreciable 6-methoxyl substituent effects are the shielding of C_7 by 23.3 ppm and the deshielding of C_6 by 31.2 ppm. A 5-methoxyl group has an entirely similar influence, shielding C_{4a} by 14.8 ppm and deshielding C_5 by 14.7 ppm. Since the apical carbons (C_{2a}, C_{8b}) are little changed in their relative positions by such methoxyl substitution, the electronegativity of ether oxygen and its ability to enter into resonance interaction with the β vinyl carbon are seen to be the dominant changes.

Clearly, whatever diamagnetic ring current may be associated with the peripheral 10 π electrons of these elassovalenes

Table IV. Summary of ^{13}C NMR Chemical Shift Data (22.6 MHz, $CDCl_3$, ppm)

Carbon	**2**	**21**[a]	**28**[b]
1	133.9[c]	136.7[c]	131.1[c]
2	115.0	111.1[d]	123.1
2a	55.3	55.6	55.1
3	115.0	113.9[d]	113.8
4	133.9[c]	132.8[c]	136.1[c]
4a	136.4	139.9[e]	121.6
5	130.8[c]	131.0[c]	145.7
6	127.5	158.7	128.6[c]
7	127.5	104.2	129.7[c]
8	130.8[c]	131.1[c]	130.1[c]
8a	136.4	133.7[e]	141.0
8b	46.4	46.3	43.3

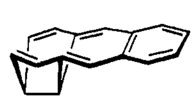
[a] Methoxyl carbon appears at 55.1 ppm. [b] Methoxyl carbon appears at 60.0 ppm. [c] Interchangeable assignments. [d] Interchangeable assignments. [e] Interchangeable assignments.

can be expected to be most apparent in the apical carbon shifts. But substantiation of this phenomen (if present) is difficult, for attempts to generate model systems could obviously result also in sufficient stereochemical and strain perturbation of these atomic centers to render the comparisons of little value.

Diamagnetic Susceptibility Measurements. Any assessment of the homoaromatic character of elassovalene (**2**) is perforce based upon differences between its observed properties and those of model compounds. Given the inherent difficulties in correlating ^1H and ^{13}C NMR shift data, our attention was directed to diamagnetic susceptibility anisotropy. The virtues of this technique for the estimation of aromatic character have been extensively discussed;[59] however, it remains unclear how well diamagnetic susceptibility data will correlate in a universal sense with other criteria of aromaticity.[60-62]

The diamagnetic susceptibilities of **2, 3**, annulated cycloheptatriene **36**, benzoelassovalene **37**,[18] and semibullvalene **38**[18] were determined alongside that of 1,6-dimethylcycloheptatriene (**39**) using the technique of direct mass suscepti-


36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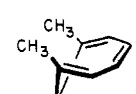
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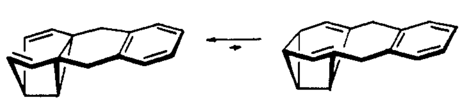
38

bility measurement of a Faraday balance[59] in order to bypass density determinations. The exaltation data so measured for these hydrocarbons are given in Table V together with estimated values based upon Haberditzl semiempirical increments[63] (χ_M'; see Experimental Section). The error limits for **2** proved to be larger than normal, probably because of air oxidation during the determinations.

Estimates of aromatic character based upon resultant net exaltations (Λ) have been reported.[59] For such true polyolefins as cyclooctatetraene, [16]annulene, heptalene, and heptafulvalene, zero exaltation is seen. This is not the case for cycloheptatriene (Λ equal to 59% of the benzene value),[59] **36**, or **39** which exhibit significant exaltations on the order of 8-11. Dauben and co-workers early concluded that conjugation is present in such systems as a result of "overlap by the indented π-orbitals of the 1- and 6-carbon atoms in the slightly buckled ring,"[59] i.e., homoaromatic character. In the present instance, the relationship between **37** and **38** is most impressive. The benzoannulated semibullvalene should exhibit no significant

Table V. Diamagnetic Exaltation Data

Compound	χ_M[c]	χ_M'[c]	Λ
2	127 ± 16	85.7	41.3
3[a]	111.9	75.1	36.8
36	103.1	92.2	10.9
37	152.1 ± 1.6	122.8[b]	29.3
38	139.0 ± 1.8	139.6[b]	−0.6
39[a]	84.3	76.0	8.3

[a] Data taken from ref 59, but reproduced in the present study as well. [b] Exaltation due to benzene ring is included in χ_M' and not Λ. [c] 10^{-6} cm^3 mol^{-1}.

exaltation, and it does not. In contrast, benzoelassovalene (**37**) exhibits a rather large Λ, a property shared by elassovalene (**2**) itself and methano[10]annulene (Table V).

Since Λ appears to be a function of the size of the aromatic (and likely also homoaromatic) system, the larger diamagnetic susceptibility exaltations found for elassovalene and its benzolog should not necessarily be construed as indicators of extensive homoaromatic delocalization. What seems certain is that the effects present in cycloheptatriene derivatives continue to be manifested in **2** and **37** (but not **38**). It is not entirely clear whether the conjugative overlap has been enhanced or not; recourse to x-ray structure analysis should provide a more direct measurement of this parameter.

Photoelectron Spectroscopic Studies and Discussion. Elassovalene might be thought of as a fractured methano[10]annulene and be expected to exhibit some of the peripheral π-electron delocalization of this aromatic system. The effect should be reduced correspondingly by a substantial degree, but one might argue that it is not reduced to nil. Alternatively, one might visualize **2** to be a relatively open polyolefin such that conjugative electronic transmission across the space separating C_2 from C_3 is nonexistent. In this instance, the structural features of the hydrocarbon would still be such that maintenance of bridged cycloheptatrienyl character would be retained. On this basis, the increase in the number of available π electrons from 6 to 10 would not be paralleled by a change from a smaller homo-Hückel ring structure to a larger one. The two descriptions therefore differ in the extent to which the canted pπ orbital at C_2 can interact with its counterpart at C_3.

Although the question of homoconjugative overlap is an important one which continues to attract theoretical scrutiny,[64] one must be careful to avoid misunderstanding of the concept. We first turn to naphthalene for which calculations indicate a C_9, C_{10} bond order of 0.518, showing negligible pπ interaction in this region despite the fully parallel nature of these orbitals.[65] In methano[10]annulene **3**, the C_1, C_6 pπ lobes are canted toward each other on the upper surface of the molecule as drawn. Despite the nonplanarity of this structure, some 1,6-overlap is necessary to rationalize both its electronic[12] and photoelectron spectra.[11] The latter study requires $\beta_{1,6}$ to be −2.0 eV with two of the five π orbitals not affected by this 1,6-interaction. The experimental ionization potentials of elassovalene (7.46, 8.33, 9.87, and 10.91 eV) similarly correlate well with Hückel calculations in which $\beta_{4a,8a} = -2.0$ eV. On this basis, the homoconjugative interactions in the central portions of **2** appear to be of approximately the same order as in **3**. For comparison purposes, the well-resolved IP's of **39** appear at 8.11, 9.04, and 10.56 eV, while those of annulated cycloheptatriene **36** are seen as a broad absorption having weak maxima at 8.10, 8.27, and 8.47 eV.

These findings infer that at distances up to at least 2.25 Å, there can be expected a reasonable degree of overlap between *one surface* of the p lobes on those carbons at the base of the methano bridge. The gap can in principle be enlarged if the tilting of the orbitals is still more accentuated. Increasing levels of σ contribution to carbon hybridization will of course materialize simultaneously.

Previously, we have argued that the preferential adoption by a substantial number of molecules of bridged cycloheptatriene rather than 1,6-dimethylenecyclohepta-2,4-diene forms is due not only to strain contributions, but also in substantial part to electronic factors.[66] Jones likewise has attributed such behavior to "a gain in homoaromaticity".[67] This assessment requires that electronic effects comparable to those present in **2** and **3** be operative also in simple cycloheptatrienes.

The present evidence points rather convincingly to the existence in elassovalene of 6 π homoaromatic interaction localized in its cycloheptatrienyl part structure. Experimental data sufficiently adequate to rule out or confirm more extensive delocalization in **2** have not been obtainable. It was for this reason that a more crystalline benzo-fused homolog was prepared and its x-ray crystal structure determined.[18]

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; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 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, Herlev, Denmark. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

2a,8b-Dihydrocyclopent[*cd*]azulene (Elassovalene, 2). A. Hydrolysis–Oxidation of 1a,2,7,7a-Tetrahydro-*N*-phenyl-1,2a,6a,-metheno-1*H*-cyclopropa[*b*]naphthalene-2,7-biimine-8,9-dicarboximide (6). A magnetically stirred mixture of **6** (0.70 g, 2.12 mmol)[4g] and potassium hydroxide (1.35 g, 25 mmol) in 2-propanol (23 mL) was refluxed under nitrogen for 30 min, cooled in ice, and brought to pH 2 with 3 *N* hydrochloric acid. After being stirred for 5 min, this mixture was treated with 3 *N* ammonium hydroxide until attainment of pH 8. After the addition of pentane (25 mL), manganese dioxide (2.0 g, 23 mmol)[37] was introduced and the mixture was stirred for 1 h at 0 °C before being allowed to warm to room temperature. After filtration, the filtrate was diluted with water (30 mL), the layers were separated, and the aqueous phase was extracted with pentane (20 mL). The combined pentane layers were washed with water (3 × 20 mL), dried, filtered, and evaporated to leave an oily residue. Careful bulb-to-bulb distillation (90 °C (0.5 mm)) yielded 228 mg (70%) of **2** which was slightly contaminated with aniline. A pure sample was obtained by preparative VPC on (9:1) 10% SF-96/KOH (4 ft × 0.25 in., Chromosorb W, 65 °C); crystallization from methanol at low temperature gave fine needles, mp 7–8 °C; ν_{max}^{neat} 2900, 2880, 1620, 1260, 1100, 905, 860, 835, 830, 760, and 685 cm^{-1}; $\lambda_{max}^{isooctane}$ 249 (ϵ 31 000) and 335 nm (2800); $\delta_{TMS}^{CDCl_3}$ 6.72 (A_2B_2 pattern, $J_{6,7}$ = 11.0 Hz, $J_{5,6} = J_{7,8}$ = 6.5 Hz, H_6 and H_7), 6.45 (m, $J_{1,2} = J_{3,4}$ = 5.3 Hz, H_1, H_4, H_5, and H_8), 6.02 (dd, J = 5.3 and 2.4 Hz, H_2 and H_3), 3.77 (d of t, J = 7.5 Hz, H_{2a}), and 1.78 (d, J = 7.4 Hz, H_{8b}); ^{13}C NMR ($CDCl_3$) 136.4, 133.9, 130.8, 127.5, 115.0, 55.3, and 46.4 ppm; *m/e* 154.0780 (calcd 154.0782).

B. Hydrolysis–Elimination of Dimesylate 7; Oxidation by Copper(II). To a stirred slurry of 450 mg (4.0 mmol) of potassium *tert*-butoxide in 10 mL of anhydrous dimethyl sulfoxide and 0.1 mL of water was added under argon 200 mg (0.38 mmol) of dimesylate **7**.[4i] The mixture, which immediately turned dark brown, was stirred for 30 min at ambient temperature, poured into 80 mL of ice water, and treated with a solution of 2.0 g of copper(II) chloride in 80 mL of water containing 1 mL of concentrated hydrochloric acid and buffered to pH 3 with sodium acetate. The expected copper complex did not form but gas evolution was evidenced. The solution was made basic (pH 9) by the addition of potassium hydroxide. Pentane (20 mL) was added and the mixture was stirred for 30 min at room temperature. The pentane layer was drawn off and the aqueous solution was rinsed with pentane (5 × 20 mL). The organic extracts were combined, rinsed with water (5 × 20 mL), dried, and filtered. The solvent was removed by careful distillation under argon. Preparative VPC (2 ft × 0.25 in. 6% QF1 on Chromosorb G, 115 °C) gave 40 mg of **2** which was identical in all respects with the above sample.

C. Hydrolysis–Elimination of Dimesylate 7; Air Oxidation. The hydrolysis was carried out as above on the same scale; however, after the reaction mixture had been poured into ice water, the aqueous phase was extracted with pentane (25 mL) and ether (4 × 25 mL). No precautions were taken to exclude air. The combined organic solutions were rinsed with water (5 × 20 mL) and brine, dried, and filtered. Evaporation of solvent in vacuo (no heat) returned a brownish oil which exhibited an NMR spectrum identical with that of **2**.

Tricarbonylelassovalenechromium (12). A mixture of **2** (180 μL, ~0.96 mmol) and tricarbonyltriamminechromium (360 mg, 1.93 mmol)[20] in degassed hexane (40 mL) was refluxed under nitrogen with stirring for 52 h. The dark red reaction mixture was cooled and filtered. The cake was washed with hexane and the washings were combined with the original filtrate. The hexane solution was concentrated and cooled to yield 52 mg of dark red crystals. Because much of the remaining material was unchanged **2** (^1H NMR analysis), it was heated as before with 175 mg of tricarbonyltriamminechromium. An additional 49 mg of **12** was isolated (total yield, 36.2%). An analytical sample of the complex was obtained by sublimation (90 °C (0.01 mm)) followed by repeated recrystallization from chloroform–hexane; mp 183–185 °C (sealed tube); $\nu_{max}^{CHCl_3}$ 1960, 1900, and 1880 cm^{-1}; λ_{max}^{hexane} 225 sh (ϵ 41 000), 229 (43 800), 355 (5680), and 470 nm (2540); $\delta_{TMS}^{CDCl_3}$ 6.16 (m, 2), 5.72 (m, 2), 5.4 (s, 4), 4.26 (m, 1), and 2.16 (d, J = 8 Hz, 1); *m/e* 290.0030 (calcd 290.0035).[68]

Anal. Calcd for $C_{15}H_{10}CrO_3$: C, 62.07; H, 3.47. Found: C, 61.73; H, 3.59.

Regeneration of 2 from 12. A mixture of **12** (64 mg) and redistilled diethylenetriamine was heated at 100 °C with stirring under nitrogen for 30 min. After cooling, water was added and the product was extracted into ether. The ethereal solution was washed with water, dried, and evaporated to leave an oil, the ^1H NMR spectrum of which was identical with that of pure **2**.

1,2,3,6,6a,6b,6c,6d-Octahydro-3β-hydroxyl-*N*-phenylbenzo[1,3]-cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentaleno-1,6-biimine-7,8-dicarboximide (13). A solution of 1.20 g (3.70 mmol) of diazasnoutane **5**[4e] and 0.10 g of rose bengal in 400 mL of anhydrous methanol was irradiated for 21 h with a Sylvania DYV tungsten halogen lamp while a slow stream of oxygen was bubbled through the solution. The reaction mixture was transferred to a 1-L round-bottom flask and cooled in ice. Following portionwise addition of 1.00 g (26.4 mmol) of sodium borohydride, the solution was stirred at room temperature for 30 min and treated with 10 mL of 4 N potassium hydroxide solution. The resultant mixture was concentrated in vacuo, diluted with water (150 mL) and chloroform (100 mL), and separated into two layers. The aqueous phase was rinsed with chloroform (4 × 100 mL) and the combined organic extracts were washed with water and brine, dried, filtered, and evaporated to leave a pink, frothy solid (~100%). Chromatography of this material on 24 g of silica gel returned 0.48 g of unreacted **5** (chloroform elution) and 0.73 g (95% based on recovered **5**) of allylic alcohol **13** (acetone–chloroform (1:1) elution). Recrystallization from chloroform–pentane provided pure **13** as a white solid, mp 206–208 °C; ν_{max}^{KBr} 1760, 1695, 1500, 1410, 1135, and 1110 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.55–7.22 (m, 5), 5.88 (dd, J = 10.0 and 2.0 Hz, 1), 5.46 (d, J = 10.0 Hz, 1), 5.18–4.90 (m, 2), 3.70 (m, 1), 3.25 (d, J = 6.0 Hz, 1), and 2.60–1.15 (br m, 6); *m/e* 347.1275 (calcd 347.1270).

Anal. Calcd for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.01; H, 5.05; N, 11.82.

Epoxidation of 5. To a magnetically stirred solution of **5** (515 mg, 1.55 mmol) in dichloromethane (20 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (380 mg of 84% purity, 1.85 mmol) in the same solvent (10 mL). The mixture was stirred overnight at room temperature, washed with sodium bisulfite (10%) and sodium carbonate (10%) solutions and brine, dried, filtered, and evaporated. Two recrystallizations of the solid residue from chloroform–hexane gave 306 mg of **15**. The combined mother liquors were chromatographed on alumina TLC plates using chloroform–acetone (9:1) as eluent. There was obtained an additional 144 mg of **15** (total yield, 84%) and 38 mg (7%) of **14**.

For **14**: mp 209.5–210.5 °C (from chloroform–ether); $\nu_{max}^{CHCl_3}$ 1755 and 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.70–7.25 (m, 5), 4.83 (dd, J = 3.0 and 2.5 Hz, 2), 2.92 (br s, $W^{1/2}$ = 5 Hz, 2), 2.60 (d, J = 16.5 Hz, 2), 2.25–1.80 (m, 5), and 1.36 (d, J = 4.0 Hz, 1).

Anal. Calcd for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 68.72; H, 5.03; N, 12.01.

For **15**: mp 221–222 °C (from chloroform–hexane); $\nu_{max}^{CHCl_3}$

1760, 1745, and 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.76–7.27 (m, 5), 4.79 (dd, J = 3.5 and 3.0 Hz, 2), 3.02 (br s, $W^{1/2}$ = 4 Hz, 2), 2.50 (d, J = 16 Hz, 2), and 2.34–1.70 (m, 4).

Anal. Calcd for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 68.73; H, 4.93; N, 12.10.

Bromohydrin Formation from 5. To an ice-cold magnetically stirred solution of **5** (1.0 g, 3.0 mmol) in 1,2-dimethoxyethane–water (9:1, 20 mL) was added dropwise a solution of *N*-bromosuccinimide (650 mg, 3.65 mmol) in 1,2-dimethoxyethane (10 ml). The resulting mixture was stirred at room temperature for 2.5 h, treated with sodium bisulfite solution (10%, 2.5 mL), and evaporated. The residue was dissolved in chloroform (100 mL), washed with brine, dried, filtered, and evaporated. The residue was twice recrystallized from chloroform–ether to give 755 mg of **16.** The combined mother liquors were chromatographed on silica gel (30 g) using chloroform and chloroform–acetone (97:3) as eluents. There were obtained an additional 140 mg of **16** (total yield, 70%) and 194 mg (15%) of **17.**

For **16:** mp 221–222 °C (from chloroform–ether); ν_{max}^{Nujol} 3480, 1750, and 1670 cm^{-1}; $\delta_{TMS}^{DMSO-d_6}$ 7.46 (s, 5), 5.33 (d, J = 4.5 Hz, 1), 5.14–4.90 (m, 2), 4.2–3.4 (m, 2), and 2.85–1.70 (br m, 8).

Anal. Calcd for $C_{20}H_{18}BrN_3O_3$: C, 56.09; H, 4.23; N, 9.81. Found: C, 55.82; H, 4.27; N, 9.71.

For **17:** mp 218–219 °C (from chloroform–ether); $\nu_{max}^{CHCl_3}$ 3585, 3430, 1750, and 1685 cm^{-1}; $\delta_{TMS}^{DMSO-d_6}$ 7.50 (s, 5), 5.30 (d, J = 4.5 Hz, 1), 5.09–4.85 (m, 2), 4.18–3.38 (m, 2), and 2.76–1.70 (br m, 8).

Anal. Calcd for $C_{20}H_{18}BrN_3O_3$: C, 56.09; H, 4.23; N, 9.81. Found: C, 55.94; H, 4.22; N, 9.81.

Cyclization of 16. A 100-mg sample of sodium hydride in oil (57%) was washed three times with pentane and slurried in anhydrous tetrahydrofuran (25 mL). Bromohydrin **16** (875 mg, 2.02 mmol) was added and the mixture was refluxed under nitrogen overnight prior to cooling in ice. After the addition of ammonium chloride solution (10%, 2 mL), the solvent was evaporated and the residue was dissolved in chloroform before washing with brine. After drying and evaporation, there remained 693 mg (98%) of pure **14,** identical in all respects with the sample prepared earlier.

Cyclization of 17. Reaction of **17** (65 mg, 0.15 mmol) with sodium hydride (20 mg of 57%) in dry tetrahydrofuran (5 mL) in the predescribed fashion furnished 45 mg (87%) of pure **15,** mp 221–222 °C.

Ring Opening of 15. A. With Basic Alumina. To a slurry of Woelm Activity I basic alumina (18 g) in anhydrous benzene (50 mL) was added 600 mg (1.73 mmol) of **15.** The mixture was stirred at room temperature for 24 h and poured directly onto the top of a short alumina column. Elution with chloroform–acetone (1:1) afforded a solid which was rechromatographed on Florisil (elution with the same solvent system) to furnish pure **18** (228 mg, 38%), mp 138–145 °C (variable because of concomitant dehydration); $\nu_{max}^{CHCl_3}$ 3600, 3450, 1750, and 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.60–7.25 (m, 5), 6.23 (d, J = 10 Hz, 1), 5.72 (dd, J = 10 and 6 Hz, 1), 5.22–4.87 (m, 2), 4.38–3.98 (br m, 1), and 2.42–1.75 (br m, 6).

Anal. Calcd for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 68.64; H, 5.05; N, 11.95.

B. With Phenylselenide Anion. To a yellow solution of diphenyl diselenide (250 mg, 0.80 mmol) in absolute ethanol (7 mL) was added 65 mg (1.71 mmol) of sodium borohydride in several batches under nitrogen. When the solution became colorless, epoxide **15** (500 mg, 1.44 mmol) was introduced followed by 14 mL of tetrahydrofuran. Heating at the reflux temperature was maintained for 5 h prior to cooling in ice and dropwise addition of 30% hydrogen peroxide (2 mL). The mixture was stirred overnight at room temperature and insoluble material separated by filtration. The filtrate was concentrated, diluted with chloroform, washed with sodium carbonate solution (10%, 3 × 20 ml) and water, dried, and again evaporated. Recrystallization of the residue from chloroform–ether gave 425 mg (85%) of **18.**

Ring Opening of 14. From reaction of 175 mg (0.55 mmol) of diphenyl diselenide, 45 mg (1.18 mmol) of sodium borohydride, and 350 mg (1.01 mmol) of **14** under the conditions described above, there was isolated 297 mg (84%) of **13,** identical in all respects with the product of photooxygenation.

1,2,3,6,6a,6b,6c,6d-Octahydro-*N*-phenyl-3-oxobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (19a). A suspension of 0.67 g (1.94 mmol) of alcohol **13** and 4.0 g (46 mmol) of activated manganese dioxide[37] in 125 ml of dichloromethane was stirred under anhydrous conditions at ambient temperature for 18 h. Filtration of the mixture through Celite and evaporation of solvent gave 0.54 g (80.6%) of crude **19a.** Filtration through alumina and recrystallization from chloroform–pentane afforded pure enone as a white solid, mp 214–215 °C; ν_{max}^{KBr} 1770, 1710, 1500, 1410, 1280, and 1135 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.28 (br s, 5), 6.98 (d, J = 9.0 Hz, 1), 5.68 (d, J = 9.0 Hz, 1), 5.12 (d, J = 4.0 Hz, 1), 4.96 (d, J = 4.0 Hz, 1), 2.84 (ABq, J_{AB} = 18.0 Hz, $\Delta\nu_{AB}$ = 12.6 Hz, 2), and 2.08 (m, 4); *m/e* 345.1113).

Anal. Calcd for $C_{20}H_{15}N_3O_3$: C, 69.55; H, 4.38; N, 12.17: Found: C, 69.16; H, 4.41; N, 11.93.

1,2,3,6,6a,6b,6c,6d-Octahydro-*N*-methyl-3-oxobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (19b). In a process which duplicated the preparation of **13,** 2.00 g (7.44 mmol) of diazasnoutane **24**[69] was photooxygenated using 0.10 g of rose bengal in 400 mL of anhydrous methanol and treated subsequentlv with 3.00 g (80.0 mmol) of sodium borohydride. After workup, chromatography on 30 g of silica gel gave 0.43 g of unreacted **24** (chloroform elution) and 1.56 g (94% based on recovered **24**) of syn allylic alcohol (1:1 acetone–chloroform elution). Recrystallization from chloroform–ether gave pure product as a white solid, mp 194.0–195.0 °C; ν_{max}^{KBr} 3410, 1755, 1685, and 1465 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.90 (dd, J = 10 and 2 Hz, 1), 5.48 (d, J = 10 Hz, 1), 4.93 (br t, J = 4.0 Hz, 2), 4.1–3.8 (m, 1), 3.03 (s, 3), and 2.7–1.3 (m, 7); *m/e* 285.1119 (calcd 285.1113).

Anal. Calcd for $C_{15}H_{15}N_3O_3$: C, 63.16; H, 5.26; N, 14.74. Found: C, 63:13; H, 5.29; N, 14.64.

To a mechanically stirred, nitrogen-blanketed solution of anhydrous pyridine (11.10 g, 141 mmol) in 400 ml of dichloromethane was added portionwise 7.00 g (70.0 mmol) of powdered dry chromium trioxide. After ca. 30 min, a solution of 3.62 g (12.7 mmol) of the allylic alcohol in 100 mL of dichloromethane was added dropwise to the deep burgundy solution. A black tar formed immediately; after 45 min, the mixture was filtered through Celite. The dark organic solution was washed with 10% sodium hydroxide solution (4 × 50 mL). Further washing with 5% hydrochloric acid, 10% sodium bicarbonate solution, and brine, followed by drying, filtration, and evaporation gave 3.34 g (93%) of enone **19b** as a white solid, mp 196.0–197.5 °C (from dichloromethane–ether); ν_{max}^{KBr} 1765, 1695, 1460, and 1395 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.11 (d, J = 10.0 Hz, 1), 5.77 (d, J = 10.0 Hz, 1), 5.17 (br d, J = 4.0 Hz, 1), 4.97 (br d, J = 5.0 Hz, 1), 3.05 (s, 3), 2.88 (ABq, J_{AB} = 18.5 Hz, $\Delta\nu_{AB}$ = 10.3 Hz, 2), and 2.40–1.95 (m, 4); *m/e* 283.0961 (calcd 283.0957).

1,6,6a,6b,6c,6d-Hexahydro-3-methoxy-*N*-methylbenzo[1,3]-cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (20). A solution of 2.00 g (7.05 mmol) of **19b,** 10.0 g (94.3 mmol) of trimethyl orthoformate, and 1.00 g (110 mmol) of oxalic acid in 160 mL of 1,2-dichloroethane–methanol (1:1) was stirred at the reflux temperature under nitrogen for 18 h. The cooled solution was evaporated to dryness. The white residue was taken up in chloroform (200 ml) and washed with 10% sodium bicarbonate solution and brine. After drying and filtration, the solution was evaporated to give 2.75 g of oil. Chromatography of this material on silica gel (ether elution) furnished 1.87 g (90%) of methoxy diene **20** as a white solid, mp 189.5–192.0 °C (sealed tube) (from ethyl acetate–ether); ν_{max}^{KBr} 1760, 1710, 1695, 1645, 1460, 1395, 1235, and 800 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.20 (d, J = 9.5 Hz, 1), 5.70 (dd, J = 9.5 and 2.0 Hz, 1), 5.05 (d, J = 2.0 Hz, 1), 5.00 (m, 2), 3.53 (s, 3), 2.95 (s, 3), 2.37 (m, 1), 2.00 (m, 2), and 0.63 (d, J = 2.5 Hz, 1).

Anal. Calcd for $C_{16}H_{15}N_3O_3$: C, 64.64; H, 5.09; N, 14.13. Found: C, 64.66; H, 5.10; N, 14.27.

2a,8b-Dihydro-6-methoxycyclopent[*cd*]azulene (6-Methoxyelassovalene, 21). With strict adherence to the procedure outlined for the preparation of **2,** 594 mg (2.00 mmol) of **20** was hydrolyzed with 800 mg (20.0 mmol) of powdered sodium hydroxide and 40 ml of 2-propanol and oxidized with 1.74 g (20.0 mmol) of activated manganese dioxide and 75 mL of pentane. Workup as before gave 303.5 mg (82.5%) of **21** as a bright yellow solid, mp 23–27 °C, after molecular distillation (40–50 °C (3.5 × 10^{-4} mm); ν_{max}^{KBr} 2910, 1625, 1510, 1455, 1400, 1255, 1220, 1145, 1020, 850, 830, and 805 cm^{-1}; $\lambda_{max}^{isooctane}$ 247 (ϵ 54 000) and 327 nm (4000); $\delta_{TMS}^{CDCl_3}$ 6.43 (dd, $J_{1,2}$ = 5.2 Hz, $J_{1,2a}$ = 2.7 Hz, H_1), 6.39 (dd, $J_{3,4}$ = 5.2 Hz, $J_{2a,4}$ = 2.7 Hz, H_4), 6.30 (dd, $J_{7,8}$ = 6.5 Hz, $J_{5,8}$ = 1.5 Hz, H_8), 6.24 (br s, H_5), 6.11 (dd, $J_{2a,3}$ = 2.7 Hz, $J_{3,4}$ = 5.2 Hz, H_3), 6.04 (dd, $J_{7,8}$ = 6.5 Hz, $J_{5,7}$ = 1.5 Hz, H_7), 5.93 (dd, $J_{2,2a}$ = 2.7 Hz, $J_{1,2}$ = 5.2 Hz, H_2), 3.90 (m, H_{2a}) 3.68 (s, 3), and 2.03 (d, $J_{2a,8b}$ = 7.5 Hz, H_{8b}). Spin decoupling: saturation at 3.90 collapsed the peak at 2.03 to a broad singlet, the peaks at 5.93 and 6.11 to doublets, $J_{1,2} = J_{3,4} = 5.2$ Hz, and the peaks at 6.39 and 6.43 to doublets with the same coupling constants. Double irradiation at 5.93 or 6.11 simplifies the signal at 3.90 to a broad doublet, $J_{2a,8b} = 7.5$ Hz; ^{13}C NMR (ppm, $CDCl_3$) 158.65 (s, C_6), 139.85 (s, C_{4a}), 136.66 (d, C_1), 133.67 (s, C_{8a}), 132.81 (d, C_4), 131.05 (d, C_8 or C_5), 130.95 (d, C_5 or C_8), 113.87 (d, C_3), 111.14 (d, C_2), 104.18 (d, C_7), 55.63 (d, C_{2a}), 55.14 (q, methyl), and 46.32 (d, C_{8b}); *m/e* 184.0891 (calcd 184.0888).

Collins Oxidation of 5. To a mechanically stirred solution of dry pyridine (7.12 g) in dichloromethane (120 mL) was added dry chromic anhydride (4.5 g, 45 mmol) under a nitrogen atmosphere. After 15 min, a solution of **5** (1.0 g, 3.0 mmol) in dichloromethane (10 mL) was added in one portion. The resulting mixture was stirred at room temperature for 12 h, treated with additional oxidant (from 4.75 g of pyridine, 3.0 g of chromic anhydride and 80 mL of dichloromethane), and stirred for an additional 12 h. The supernatant was decanted through glass wool into a separatory funnel. The insoluble residue was washed with dichloromethane (2 × 50 mL) and the combined organic layers were washed with sodium hydroxide (5%, 150 mL), hydrochloric acid (5%, 150 mL), sodium bicarbonate (5%, 150 mL), and saturated brine solutions (150 mL), dried, filtered, and evaporated. The crude mixture (505 mg) was chromatographed on silica gel (30 g) using chloroform–acetone (98:2) as eluent and afforded 102 mg of unreacted **5** and a mixture of **22a** and **23.** The latter mixture was separated by preparative TLC to give 47 mg (3%) of **23** and 210 mg (23%) of **22a.**

For **22a:** mp 204–205 °C (from chloroform–hexane); $\nu_{max}^{CHCl_3}$ 1760, 1700, and 1665 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.70–7.20 (m, 5), 6.59 (d of t, J = 10 and 4 Hz, 1), 5.97 (d of t, J = 10 and 2 Hz, 1), 5.78 (d, J = 5 Hz, 1), 5.07 (d, J = 5 Hz, 1), 2.87 (dd, J = 4 and 2 Hz, 2), and 2.50–1.84 (m, 4).

Anal. Calcd for $C_{20}H_{15}N_3O_3$: C, 69.55; H, 4.38; N, 12.17. Found: C, 69.60; H, 4.38; N, 11.88.

For **23:** mp 247.5–248.5 °C (from chloroform–ether); $\nu_{max}^{CHCl_3}$ 1778, 1710, 1680, and 1595 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.67–7.32 (m, 5), 6.62 (s, 2), 5.91 (t, J = 3 Hz, 2), 3.27 (d, J = 4 Hz, 1), and 2.50–2.15 (m, 3).

Anal. Calcd for $C_{20}H_{13}N_3O_4$: C, 66.85; H, 3.65; N, 11.70. Found: C, 66.61; H, 3.84; N, 11.69.

1,2,5,6,6a,6b,6c,6d-Octahydro-*N*-methyl-2-oxobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (22b). To a mechanically stirred solution of 7.12 g (225 mmol) of pyridine in 300 ml of dichloromethane in a 500-mL three-necked Morton flask fitted with a stopper and a condenser topped with an argon inlet was added portionwise 11.2 g (112 mmol) of dry chromium trioxide. The Collins reagent was stirred for 15 min, then transferred under argon via a glass adapter to a solution of 2.00 g (7.44 mmol) of diazasnoutane **24** in 10 mL of dichloromethane in an identically equipped 2-L three-necked Morton flask. The flask was stoppered and the mixture was vigorously stirred for 12 h at ambient temperature. A second addition of Collin's reagent [from 7.40 g (74.0 mmol) of chromium trioxide and 11.7 g (148 mmol) of pyridine in 200 mL of dichloromethane] was made and stirring was continued for an additional 12 h. The mixture was filtered through glass wool, and the solids were thoroughly rinsed with dichloromethane. The combined organic solutions were extracted with 10% sodium hydroxide solution (2 × 200 mL), 10% hydrochloric acid (150 mL), saturated sodium bicarbonate solution (150 mL), and brine (150 mL), dried, filtered, and evaporated to give ca. 1 g of brown oil. The inorganic solids were dissolved in base and the resulting green flocculent solid was removed by filtration. The solids were thoroughly washed with dichloromethane and the aqueous solution was rinsed with dichloromethane (4 × 150 mL). The combined organic solutions were processed as before to give an additional 1 g of tan oil. Chromatography of the combined residue on 80 g of silica gel (chloroform elution) returned 420 mg of unreacted **24** and 720 mg (43.4% based on recovered **24**) of enone. Recrystallization from ethyl acetate gave pure **22b** as a light yellow solid, mp 224.0–226.5 °C dec (sealed tube); ν_{max}^{KBr} 1760, 1700, 1660, 1455, and 1395 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.61 (dt, J = 4.0 and 10.0 Hz, 1), 5.95 (dt, J = 2.0 and 10.0 Hz, 1), 5.70 (d, J = 4.0 Hz, 1), 4.97 (d, J = 4.0 Hz, 1), 3.07 (s, 3), 2.87 (dd, J = 2.0 and 4.0 Hz, 2), 2.42 (d, J = 4.0 Hz, 1), and 2.40–190 (m, 3); *m/e* 283.0961 (calcd 283.0957).

Anal. Calcd for $C_{15}H_{13}N_3O_3$: C, 63.60; H, 4.62; N, 14.83. Found: C, 63.44; H, 4.69; N, 14.81.

4,5-Epoxydecahydro-*N*-methyl-3-oxobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (25). To a stirred solution of 283 mg (1.00 mmol) of **19b** in 100 mL of absolute ethanol was added in one portion a solution of 69 mg (0.5 mmol) of potassium carbonate and 102 mg (3.00 mmol) of hydrogen peroxide in 5 mL of water. The solution darkened slightly upon addition, became cloudy, then cleared. After 4 h, the mixture was concentrated to ca. one-third volume and diluted with 400 mL of water. The aqueous solution was extracted with chloroform (5 × 50 mL), and the combined organic layers were washed with saturated sodium bicarbonate solution and brine, dried, filtered, and evaporated. There was obtained 224.7 mg (75.2%) of epoxy ketone, recrystallization of which first from acetone–chloroform and then ethyl acetate gave pure **25** as a white solid, mp > 262 °C dec; ν_{max}^{KBr} 1765, 1755, 1710, 1690, 1460, 1400, 1255, 1245, 970, 760, and 745 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.17 (d, J = 3.0 Hz, 1), 4.87 (d, J = 3.0 Hz, 1), 3.63 (d, J = 4.5 Hz, 1), 3.13 (br s, 4), 2.88 (ABq, J_{AB} = 15.0 Hz, $\Delta\nu_{AB}$ = 26.0 Hz, 2), and 2.20–2.00 (m, 4); *m/e* 299.0910 (calcd 299.1906).

Anal. Calcd for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04. Found: C, 60.17; H, 4.50; N, 13.89.

Alternate Synthesis of 22b. A solution of 224 mg (0.75 mmol) of **25,** 1 mL of hydrazine hydrate, and 4 drops of glacial acetic acid in 15 mL of dry dioxane was heated on a steam bath for 0.5 h. The mixture was concentrated nearly to dryness and diluted with 5% hydrochloric acid. The aqueous solution was extracted with chloroform (5 × 20 mL), and the combined organic layers were washed with saturated sodium bicarbonate solution and brine, dried, filtered, and evaporated. The tan oily residue was purified by preparative thin layer chromatography to give 47.5 mg of recovered **25** and 50.0 mg (30% based on recovered **25**) of allylic alcohol **26.** This product was not characterized but was immediately oxidized with Collin's reagent.

To a nitrogen-blanketed solution of 185 mg (2.34 mmol) of dry pyridine in 10 ml of dichloromethane was added with vigorous stirring 106 mg (1.06 mmol) of dry chromium trioxide. After 20 min, the sample of **26** contained in a minimum volume of dichloromethane was added dropwise to the burgundy solution. The solution darkened with the formation of a black tar; after 15 min, the mixture was filtered through Celite. The organic solution was washed with 10% sodium hydroxide, 10% hydrochloric acid, saturated sodium bicarbonate, and brine solutions. Drying, filtration, and evaporation of solvent provided 45.3 mg (91.2%) of **22b** identical with the material synthesized above.

1,6,6a,6b,6c,6d-Hexahydro-2-methoxy-*N*-phenylbenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (27a). A solution of **22a** (534 mg, 1.55 mmol), trimethyl orthoformate (316 mg, 3.0 mmol), and *p*-toluenesulfonic acid (30 mg) in anhydrous methanol (5 mL) and 1,2-dichloroethane (5 mL) was refluxed for 2 h, cooled, and evaporated. The residue was dissolved in chloroform, washed with saturated sodium bicarbonate and brine solutions, dried, and freed of solvent. The crude product was chromatographed on silica gel (5 g) with chloroform elution to give 387 mg (68%) of **27a** as colorless crystals, mp 208–210 °C (from chloroform–ether); $\nu_{max}^{CHCl_3}$ 1765, 1750, and 1700 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.30 (s, 5), 5.96–5.56 (m, 3), 5.16–4.92 (m, 2), 3.60 (s, 3), 2.38 (dt, J = 5.0 and 4.0 Hz, 1), 2.15–1.92 (m, 2), and 0.90 (d, J = 4.0 Hz, 1).

Anal. Calcd for $C_{21}H_{17}N_3O_3$: C, 70.18; H, 4.77; N, 11.69. Found: C, 69.55; H, 4.74; N, 11.70.

1,6,6a,6b,6c,6d-Hexahydro-2-methoxy-*N*-methylbenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-1,6-biimine-7,8-dicarboximide (27b). In a process which mirrored the preparation of **20,** 243.8 mg (0.86 mmol) of **22b** was converted to methoxydiene **27b** in 68% yield by use of 40 mg of *p*-toluenesulfonic acid, 913 mg (8.60 mmol) of trimethyl orthoformate, and 10 mL of 1:1 methanol-1,2-dichloromethane. Chromatography on 5 g of silica gel with chloroform elution followed by ethyl acetate–ether recrystallization gave analytically pure **27b** as a white solid, mp 156.5–158.0 °C, ν_{max}^{KBr} 1768, 1705, 1465, 1395, 1260, 1240, 790, 750, and 725 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.40–6.10 (AB portion of ABX, $\Delta\nu_{AB}$ = 10 Hz, J_{AB} = 10.0 Hz, J_{AX} = 1 Hz, J_{BX} = 8 Hz, 2), 5.60 (m, 1), 5.20–4.90 (X portion of ABX, 1, and m, 1), 3.67 (s, 3), 3.00 (s, 3), 2.60–2.20 (m, 1), 2.20–1.80 (m, 2), and 0.90 (d, J = 4.0 Hz, 1); *m/e* 297.1119 (calcd 297.1113).

Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 64.64; H, 5.09; N, 14.13. Found: C, 64.50; H, 5.12; N, 14.07.

2a,8b-Dihydro-5-methoxycyclopent[*cd*]azulene (5-Methoxyelassovalene, 28). A. Hydrolysis–Oxidation of 27a. A solution of **27a** (245 mg, 0.68 mmol) and potassium hydroxide (390 mg, 7.0 mmol) in 2-propanol (15 mL) was heated at reflux under nitrogen for 30 min, cooled, brought to pH 2 with 3 N hydrochloric acid, and stirred for

Table VI. Estimation of Diamagnetic Susceptibility for Elassovalene (**2**) by the Haberditzl Method

Structural element	χ_M (10^{-6} cm^3 mol^{-1})
Bonds[a]	
C*-C*	$9 \times 2.4^b = 21.6$
C*-C_3	$4 \times 2.6^b = 10.4$
C_3-C_3	$1 \times 3.3^b = 3.3$
CπC	$5 \times 2.2^b = 11.0$
C*-H	$8 \times 3.2^b = 25.6$
C_3-H	$2 \times 3.5^b = 7.0$
"Core" electrons[c]	
C(1s)	$12 \times 0.15^d = 1.8$
Small rings[e]	
Cyclopentene[f]	$2 \times 2.5 = 5.0$
	$\chi_M' = 85.7$

[a] An asterisk denotes sp^2 hybridization; the numerical subscript denotes the number of carbon atoms attached to that carbon. [b] Values taken from ref 70. [c] Electrons in orbitals not available for bonding. [d] Value of J. Baudet, J. Tillieu, and J. Guy, *C. R., Acad. Sci.*, **244,** 1756 (1957). [e] Diamagnetic susceptibilities for cyclopropane and cyclopentene are somewhat underestimated by the Haberditzl method. [f] The value given is for unsubstituted cyclopentene.

Table VII. Estimation of Diamagnetic Susceptibility for **36** by the Haberditzl Method

Structural element	χ_M (10^{-6} cm^3 mol^{-1})
Bonds[a]	
C*-C*	$5 \times 2.4^b = 12.0$
C*-C_2	$4 \times 2.6^b = 10.4$
C_2-C_2	$3 \times 3.6^b = 10.8$
CπC	$3 \times 2.2^b = 6.6$
C*-H	$4 \times 3.2^b = 12.8$
C_2-H	$10 \times 3.8^b = 38.0$
"Core" electrons[c]	
C(1s)	$11 \times 0.15^d = 1.6$
	$\chi_M' = 92.2$

[a-d] See corresponding footnotes in Table VI.

Table VIII. Estimation of Diamagnetic Susceptibility for **37** by the Haberditzl Method

Structural element	χ_M (10^{-6} cm^3 mol^{-1})
Bonds[a]	
C*-C*	$14 \times 2.4^b = 33.6$
C*-C_3	$4 \times 2.6^b = 10.4$
C_3-C_3	$1 \times 3.3^b = 3.3$
CπC	$7 \times 2.2^b = 15.4$
C*-H	$10 \times 3.2^b = 32.0$
C_3-H	$2 \times 3.5^b = 7.0$
"Core" electrons[c]	
C(1s)	$16 \times 0.15^d = 2.4$
Small rings[e]	
Cyclopentene[f]	$2 \times 2.5 = 5.0$
Benzene exaltation	$1 \times 13.7^b = 13.7$
	$\chi_M' = 122.8$

[a-f] See corresponding footnotes in Table VI.

Table IX. Estimation of Diamagnetic Susceptibility for **38** by the Haberditzl Method

Structural element	$\chi_M{}^A$ (10^{-6} cm^3 mol^{-1})[g]	$\chi_M{}^B$ (10^{-6} cm^3 mol^{-1})[g]
Bonds[a]		
C*-C*	$8 \times 2.4^b = 19.2$	$8 \times 2.4^b = 19.2$
C*-C_n	$6 \times 2.6^b = 15.6$	$8 \times 2.6^b = 20.8$
C_n-C_n	$6 \times 3.3^b = 19.8$	$4 \times 3.3^b = 13.2$
CπC	$5 \times 2.2^b = 11.0$	$5 \times 2.2^b = 11.0$
C*-H	$8 \times 3.2^b = 25.6$	$6 \times 3.2^b = 19.2$
C_2-H	$4 \times 3.8^b = 15.2$	$4 \times 3.8^b = 15.2$
C_3-H	$2 \times 3.5^b = 7.0$	$4 \times 3.5^b = 14.0$
"Core" electrons[c]		
C(1s)	$16 \times 0.15^d = 2.4$	$16 \times 0.15^d = 2.4$
Small rings[e]		
Cyclopropane[h]	$1 \times 5.1 = 5.1$	$1 \times 5.1 = 5.1$
Cyclopentene[f]	$2 \times 2.5 = 5.0$	$2 \times 2.5 = 5.0$
Benzene exaltation	$1 \times 13.7^b = 13.7$	$1 \times 13.7^b = 13.7$
	$\chi_M'^A = 139.6$	$\chi_M'^B = 138.8$
$\chi_M' = 0.96\ \chi_M'^A + 0.04\ \chi_M'^B = 139.6$		

[a-f] See corresponding footnotes in Table VI. [g] At room temperature the mole fraction of valence tautomer A (cyclopropane ring positioned in the central portion of the molecule) was determined to be 0.96.[18] [h] The value given is for unsubstituted cyclopropane.

5 min. The pH of this solution was altered to 8 by addition of 3 N ammonium hydroxide. After dilution with 20 mL of dichloromethane and introduction of activated manganese dioxide (1.0 g), the mixture was stirred in an ice bath for 1 h, filtered to remove the insolubles, and diluted with water (50 mL). The aqueous layer was reextracted with dichloromethane (20 mL) and the combined organic layers were dried, filtered, and evaporated. Bulb-to-bulb distillation of the residual oil gave 48 mg of slightly contaminated **28.** Further purification by sublimation (36 °C (7×10^{-4} mm) gave **28** as a yellow solid, mp 45-50 °C; $\nu_{max}{}^{KBr}$ 1610, 1235, 1205, 1155, 795, and 745 cm^{-1}; $\lambda_{max}{}^{isooctane}$ 238 (ϵ 29 000), 262 (37 000), and 348 nm (1800); $\delta_{TMS}{}^{CDCl_3}$ 6.50-6.90 (m, AB portion of ABX similar to $\Delta\nu_{AB} = 5.0$ Hz, $J_{AB} = 8.0$ Hz, $J_{BX} = 4.2$ Hz, $J_{AX} = 1.8$ Hz, H_7, H_8, and H_4), 6.43 (dd, $J_{1,2} = 5.5$ Hz, $J_{2,2a} = 2.0$ Hz, H_2), 6.25 (d with additional splitting, $J_{1,2} = 5.5$ Hz, H_1), 6.10 (dd, $J_{3,4} = 5.5$ Hz, $J_{2a,3} = 2.0$ Hz, H_3), 5.83 (q, X portion of ABX, H_6), 3.75 (dt with additional splitting, $J_{2a,8b} = 7.5$ Hz, $J_{2,2a} = J_{2a,3} = 2.0$ Hz, H_{2a}), 3.64 (s, 3), and 1.85 (br d, $J_{2a,8b} = 7.5$ Hz, H_{8b}). Spin decoupling: saturation at δ 3.75 collapsed the signal at 1.85 to a broad singlet and the peaks at 6.10 and 6.43 to doublets, $J_{2,2a} = J_{2a,3} = 5.5$ Hz. Conversely, double irradiation at 6.10 or 6.43 simplified the multiplet at 3.75; ^{13}C NMR ($CDCl_3$) 145.67 (s, C_5), 141.04 (s, C_{8a}), 136.07, 131.06, 130.09, 129.66, and 128.58 (d, C_4, C_1, C_8, C_7, and C_6), 123.08 (d, C_2 or C_3), 121.57 (s, C_{4a}), 113.80 (d, C_3 or C_2), 60.08 (q, CH_3), 55.07 (d, C_{2a} or C_{8b}), and 43.31 ppm (d, C_{8b} or C_{2a}); *m/e* 184.0920 (calcd 184.0888).

B. Hydrolysis-Oxidation of 27b. The hydrolysis and oxidation of 396 mg (1.33 mmol) of **27b** were carried out using 534 mg (13.3 mmol) of activated manganese dioxide and 75 mL of pentane. There was isolated after sublimation (36 °C (7×10^{-4} mm) of the residue 172.4 mg (72.4%) of **28** as a bright yellow solid, mp 45-50 °C, identical with the material isolated above.

Diamagnetic Susceptibility Determinations. A given magnetic susceptibility (χ_M) was determined using

$$\chi_M = (MW)(\beta)[(\Delta W - \alpha)/W] \quad (1)$$

for the compounds shown in Table V. MW is the molecular weight of the sample, ΔW is the difference of the weight of sample in and out of the magnetic field, W is the weight of the sample, α is the difference in weight of the container in and out of the magnetic field, and β is the field strength (as computed by measurements involving standards).

Using semiempirical Haberditzl increments,[59,63] the diamagnetic susceptibility of an organic compound can be estimated on the basis of the sum of contributions from its structural parts

$$\chi_M' = \sum_i f_i \chi_i \quad (2)$$

In this expression, f_i is the number of times that a structural element of susceptibility χ_i is repeated in the molecule and there are a number of i of such increments. In Tables VI-IX, estimates are provided for **2, 36, 37,** and **38.**

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