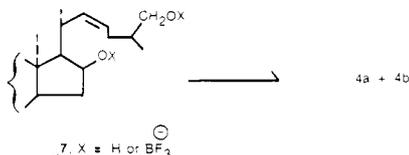


Figure 1. Perspective of 3 β ,16 β ,23(R),26-tetrahydroxy-5 β -cholestane.

involve concomitant formation of a transitory vinyl ether such as **6** that easily cleaves to olefin **7**. Addition of in situ generated diborane (hydroboration sequence) to the olefin intermediate (**7**) would proceed mainly from the least hindered carbon po-

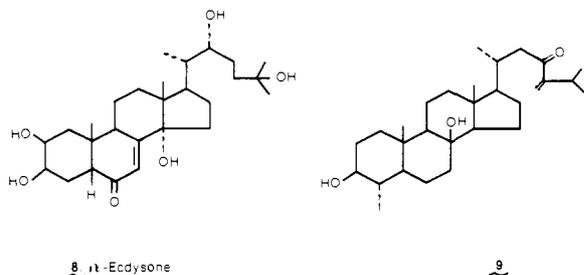


sition (and side) to yield as major product the 23R alcohol. The experimental observations, including the fact that dihydrosmilagenin (**3**) is not an intermediate in this unusual reaction, seem consistent with such a mechanistic pathway.

Single crystals of the C-23R isomer of tetraol **4b** were obtained from a saturated acetone and methanol solution. Precession photographs revealed Laué symmetry and systematically extinct reflections corresponding uniquely to monoclinic space group $P2_1$ with cell constants $a = 17.826$ (5) Å, $b = 7.682$ (2) Å, $c = 10.996$ (4) Å, and $\beta = 122.38$ (2)°. Crystal density, measured by flotation in carbon tetrachloride-toluene, was found to be 1.12 g cm^{-3} ($\rho_{\text{calcd}} = 1.14 \text{ g cm}^{-3}$, for $Z = 2$). Diffraction intensity measurements were made on a Syntex P1 four-circle diffractometer using graphite monochromated $\text{CuK}\alpha$ ($\lambda = 1.54178$ Å) radiation. Reflections were scanned in a variable speed (between 1 and 12 deg min^{-1}) 2θ - θ mode. Of 2849 reflections measured with $(\sin \theta)/\lambda < 0.50$ in one quadrant of reciprocal space, 2645 unique reflections were accepted with $|F_o| > 0$. Corrections were made for Lorentz and polarization effects but not for absorption ($\mu = 5.4 \text{ cm}^{-1}$) or extinction.

Direct methods were used to solve the structure using MULTAN-74.⁸ Large-block least-squares refinement⁹ with anisotropic thermal parameters, fixed C-H hydrogen positions (placed at idealized locations 1.0 Å from respective C atom), and variable O-H hydrogen positions (located by a difference Fourier synthesis) converged at residual $R = 0.058$ and $R_w = 0.048$, where weighted residual $R_w = (\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|^2$ and $w = 1/\sigma_{F_o}^2$. Since 3 β ,16 β ,23(R),26-tetrahydroxy-5 β -cholestane was obtained by reduction of the 5 β -cholestane, smilagenin, the absolute configuration and conformation displayed in the perspective view in Figure 1 are those of the correct enantiomer.

Naturally occurring sterols bearing oxygen at C-22 or C-23 such as the insect molting hormone α -ecdysone¹⁰ (**8**) and the



new soft coral component **9**¹¹ require extensive structural maneuvers to elaborate the necessary side-chain oxygen sub-

stituents. The unique one-step conversion of steroidal saponins to C-22 and C-23 alcohols greatly improves the accessibility of such intermediates for synthetic purposes.

Acknowledgments. We are grateful for support of this investigation by the National Cancer Institute, Public Health Research Grants CA-16049-05 from the National Cancer Institute, the Fannie E. Rippel Foundation, Mrs. Mary Dell Pritzlaff, The Olin (Spencer T. and Ann W.) Foundation, and the Phoenix Coca Cola Bottling Co.

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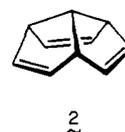
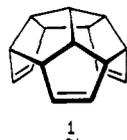
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Quantitative Assessment of pp- σ Overlap in a Topologically Convex Triene. Electronic and Crystal Structure Analysis of C₁₆-Hexaquinacene

Sir:

C₁₆-Hexaquinacene (**1**) is the third and newest member¹ of a select group of trienes, which includes triquinacene (**2**) and *cis*³-1,4,7-cyclononatriene (**3**), whose constituent double bonds adopt an arrangement potentially suitable for effective pp- σ overlap.² Thus, the question arises as to whether one or more members of this series might partake of neutral homoaromatic character.³ Photoelectron (PE) spectroscopic investigations of **3**⁴ have revealed a sizable interaction between its π bonds. The energy difference between the bands corresponding to ionization from the $\epsilon(\pi)$ and $a_1(\pi)$ orbitals was found to be 0.9 eV. This split corresponds to a resonance integral (β) of -0.3 eV, a value consistent with the distance (2.46 Å)⁵ between the ethylene units. Although the distance in **2** (2.533 Å)⁶ is close to that found for **3**, a split of only 0.35-0.4 eV has been found.⁷ This difference between **2** and **3** has been explained by hyperconjugative effects.^{7,8} Thus, in **3** the interactions of $\epsilon(\pi)$ and $a_1(\pi)$ with the σ frame are of similar magnitude, while in



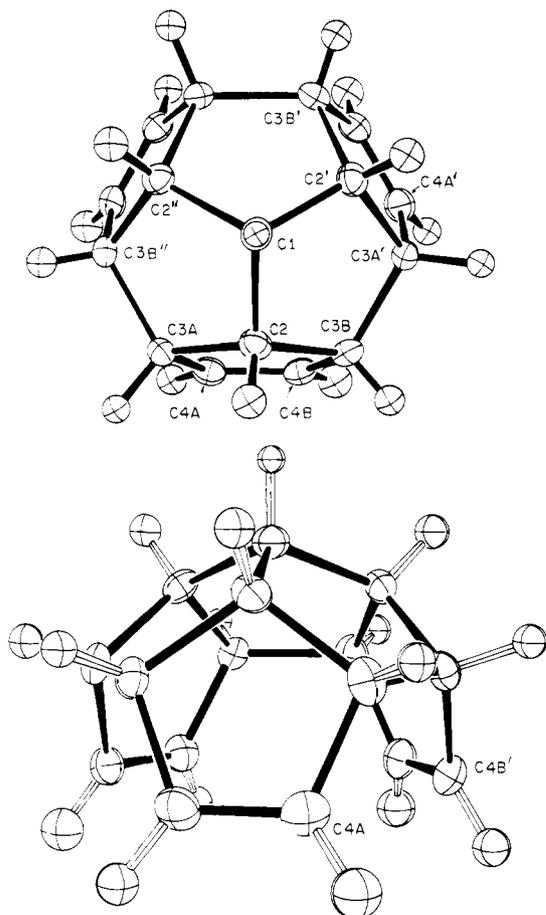


Figure 1. Top: view of C_{16} -hexaquinacene down the threefold axis showing the atomic numbering. Important bond distances and angles follow: C-1-C-2, 1.544 Å; C-2-C-3A, 1.574 Å; C-2-C-3B, 1.542 Å; C-3A-C-3B', 1.561 Å; C-3A-C-4A, 1.505 Å; C-3B-C-4B, 1.513 Å; C-4A-C-4B, 1.323 Å; C-2'-C-1-C-2, 108.0°; C-1-C-2-C-3A, 107.8°; C-1-C-2-C-3B, 109.2°; C-2-C-3B-C-3A', 107.6°; C-2-C-3A-C-3B'', 107.4°; C-3A-C-2-C-3B, 107.2°; C-2-C-3A-C-4A, 102.7°; C-2-C-3B-C-4B, 103.6°; C-3A-C-4A-C-4B, 113.5°; C-3B-C-4B-C-4A, 112.8°. Average $\sigma(C-C) \approx 0.003$ Å and $\sigma(C-C-C) \approx 0.2^\circ$. Bottom: view of the molecule perpendicular to the threefold axis emphasizing its hemispherical shape. The C-4A-C-4B' distance is 2.848 Å (see text). Thermal ellipsoids are all (including hydrogen atoms) shown at the 50% probability level.

2 the interaction of $a_1(\pi)$ with the σ frame is stronger than that involving $e(\pi)$.

The X-ray crystal structure data for **2** and **3** have provided not only the internuclear distance (R) in the gap, but also accurate information on the relative canting of the opposed p orbitals. The extent of interpenetration of these orbitals, as given by the overlap (S), has been established through vector analysis to be 0.054 and 0.066, respectively.² Models indicate that the enhanced sphericity of **1** leads to a much improved in-plane alignment of the $p\pi$ orbital triad. The important question of whether these orbitals are in adequate proximity to engage in homoconjugative stabilization is resolved herein.

That **1** does not exist as a highly delocalized ground-state molecule is already apparent in its 1H and ^{13}C NMR spectra.¹ The four carbon resonances (131.57, 60.15, 54.91, and 53.06 ppm) and the attendant $^{13}C-H$ coupling constants (160.1, 138.2, 134.3, and 137.7 Hz, respectively) appear quite normal. Its vacuum ultraviolet spectrum recorded in cyclohexane solution is characterized by a lone absorption maximum at 192 nm (ϵ 20 000), the lack of vibrational fine structure comparing favorably with the electronic spectra given by triquinacene ($\lambda_{max}^{isooctane}$ 187 nm (ϵ 13 000))^{9a} and cyclopentene (λ_{max} 180 nm (ϵ 10 000)).^{9b}

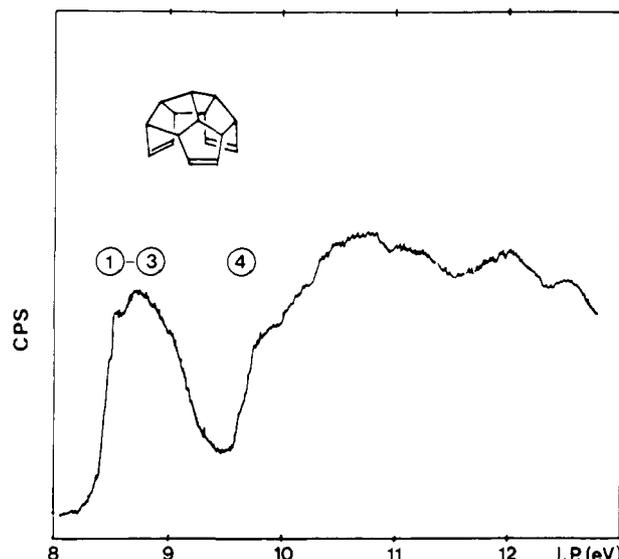


Figure 2. The He(I) photoelectron spectrum of C_{16} -hexaquinacene.

Columnar hexagonal crystals of **1**, grown from acetone solution, gave the rhombohedral cell constants $a = 7.285$ (1) Å and $\alpha = 112.59$ (1)° (λ (Mo $K\alpha$) = 0.71069 Å, $T = -107$ °C). The density and lack of systematic absences indicated probable space groups $R3$ and $R3m$. All accessible reflections with $4.0^\circ \leq 2\theta \leq 75.0^\circ$ were measured at least three times and at several different crystal settings about the scattering vector. Averaging of over 7000 low temperature (-107 °C) measurements¹⁰ gave a final data set of 595 unique reflections. Data reduction and weighting were performed in the standard way.¹¹ The structure, solved by inspection of the Patterson function and refined by conventional Fourier and least-squares techniques,¹² showed C_{16} -hexaquinacene to possess very nearly $3m$ point symmetry, although the space group is actually $R3$ (hexagonal indexing: $a = 12.122$ (1) and $c = 6.073$ (1) Å, C_3^4 , No. 146). The final disagreement indices are $R(F) = 0.062$, $R_w(F^2) = 0.062$, and $GOF = 1.92$. The final difference Fourier map (average noise level, ca. ± 0.1 e $^-/\text{Å}^3$) shows no residual electron density > 0.30 e $^-/\text{Å}^3$, with these peaks nearly all localized in the bonding regions.

Figure 1 depicts the molecular geometry and gives the bond distances and angles. The deviations from idealized $3m$ symmetry are most apparent in the bond distances about C-2, which differ by nearly 10σ . The central cyclopentane rings are planar within experimental error, but the cyclopentene rings are puckered very slightly *outward*; we observe the planar C-3A-C-4A-C-4B-C-3B olefin fragment to make a 5.4° dihedral angle with the plane defined by C-3A-C-2-C-3B. For comparison, the same angle in cyclopentene is 29.0° ,¹³ and in triquinacene (**2**), 2.2° .⁶

The intramolecular C-4B-C-4A' distance is 2.85 Å, or ~ 0.3 Å shorter than the usual 3.1-Å aromatic stacking distance. The normals to the three olefin units intersect on the threefold axis at a point 2.23 Å from the midpoints of the double bonds; the angles between these normals and the threefold axis are 107.0° .

On the basis of these findings, the magnitude of the $p-p$ overlap integral between the C-4B-C-4A' atom pair is seen to be only 0.054. Although the geometry is more favorable, the longer interatomic distances clearly have an untoward effect.

To gain a more accurate estimate of the prevailing through-space effects, the He(I) PE spectrum of **1** was determined (Figure 2) and found to exhibit a single peak separated by ~ 1 eV from strongly overlapping bands, in a manner very similar to the pattern given by **2**. Because the π units in **1** are

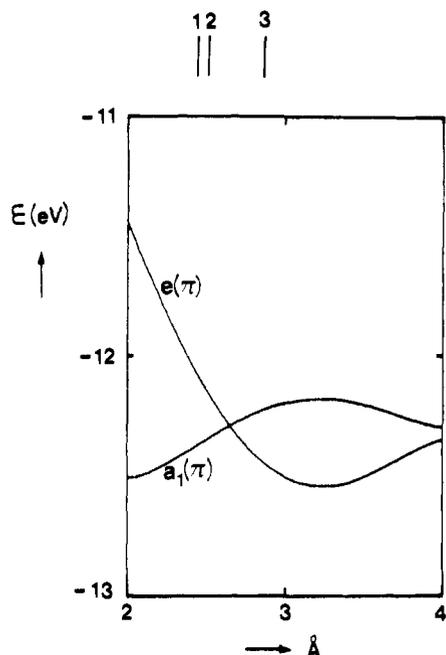


Figure 3. Orbital energy plot showing the variations in $e(\pi)$ and $a_1(\pi)$ levels as a function of distance between interacting π bonds.

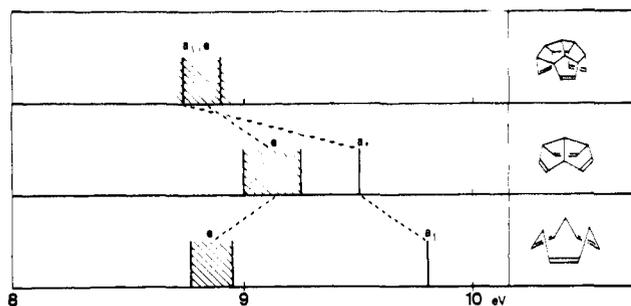


Figure 4. Correlation of the ionization energies of 1-3.

Table I. Comparison between the Ionization Potentials and Molecular Orbital Energies of C_{16} -Hexaquinacene (**1**)^a

band	I_v	assignment	$-\epsilon_j$ (MINDO/3)
①	8.74	$a_1(\pi)$	8.94
②		$e(\pi)$	9.41
③			
④	9.9	$a_2(\sigma)$	9.75

^a All values are in electron volts.

separated by 2.85 Å, the split between $e(\pi)$ and $a_1(\pi)$ should be below 0.5 eV. The first band is therefore assigned to ionization from $e(\pi)$ as well as $a_1(\pi)$ (see Table I). This assignment is supported by MO calculations of the MINDO/3 type,¹⁴ assuming the validity of Koopmans' theorem.¹⁵

These calculations predict $a_1(\pi)$ to reside above $e(\pi)$ owing to the strong interaction of $a_1(\pi)$ with $a_1(\sigma)$ as in the case of **2**. In Figure 3, we have plotted the orbital energy of $e(\pi)$ and $a_1(\pi)$ of **1** as a function of the distance between the π segments. For this purpose, extended Hückel calculations were utilized.¹⁶ Like the MINDO/3 method, this procedure predicts a crossing of $a_1(\pi)$ and $e(\pi)$ at 2.6 Å, thereby also implicating the sequence $a_1(\pi)$, $e(\pi)$ for **1**.

The ionization energies of **1-3** are correlated in Figure 4. As a result of the more extended σ framework in **1** relative to **2** and **3**, the center of gravity is shifted toward lower energy. As a direct consequence of the larger distance between its π bonds, homoconjugation in **1** is completely overridden by hyperconjugation.

The essentially ineffective σ overlap of the $p\pi$ orbitals in **1** has decided chemical ramifications. Thus, the triene is totally inert to attempted reduction with potassium in liquid ammonia or oxidation with $\text{Co}(\text{Az})_3$ in a flow-through system.¹⁷

The electronic nature of **1** would appear to rule out the likelihood that neutral homoaromatic character will ever be uncovered.

Acknowledgments. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society (G.G.C.), the National Institutes of Health (Grant AI-11490, LAP), the Deutsche Forschungsgemeinschaft (R.G.), and the Fonds der Chemischen Industrie (R.G.) for financial support. Thanks are also due Mrs. H. Roth for the PE spectral measurement and Dr. Joseph Cassim for the use of his UV spectrometer.

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$$R'' = \left[\frac{\left(\sum_{hkl} \sum_{j=1}^{n_j} w |F_j^2 - F_{av}^2| \right)}{\left(\sum_{hkl} w (\eta_j - 1) F_{av}^2 \right)} \right] = 0.049$$
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Static and Dynamic Stereochemistry of Dicoordinate Phosphorus Cations

Sir:

It has been demonstrated^{1,2} that halide ion abstraction from halophosphines results in apparently dicoordinate phosphorus