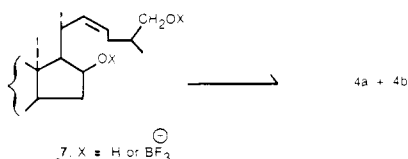


Figure 1. Perspective of 3 $\beta$ ,16 $\beta$ ,23(R),26-tetrahydroxy-5 $\beta$ -cholestane.

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-

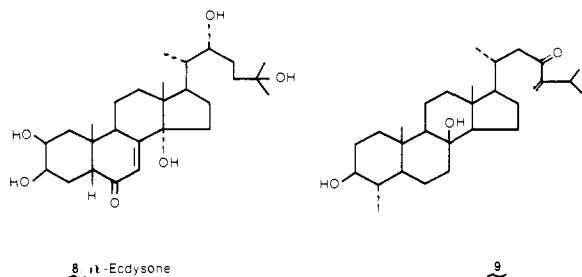


sition (and side) to yield as major product the 23R alcohol. The experimental observations, including the fact that dihydrosmilagenin (**3**) is not an intermediate in this unusual reaction, seem consistent with such a mechanistic pathway.

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  $1.12 \text{ g cm}^{-3}$  ( $\rho_{\text{calcd}} = 1.14 \text{ g cm}^{-3}$ , 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  $\text{min}^{-1}$ )  $2\theta$ - $\theta$  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.<sup>8</sup> Large-block least-squares refinement<sup>9</sup> 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 $\beta$ ,16 $\beta$ ,23(R),26-tetrahydroxy-5 $\beta$ -cholestane was obtained by reduction of the 5 $\beta$ -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  $\alpha$ -ecdysone<sup>10</sup> (**8**) and the



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

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

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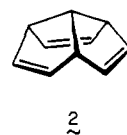
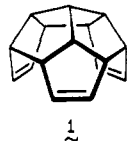
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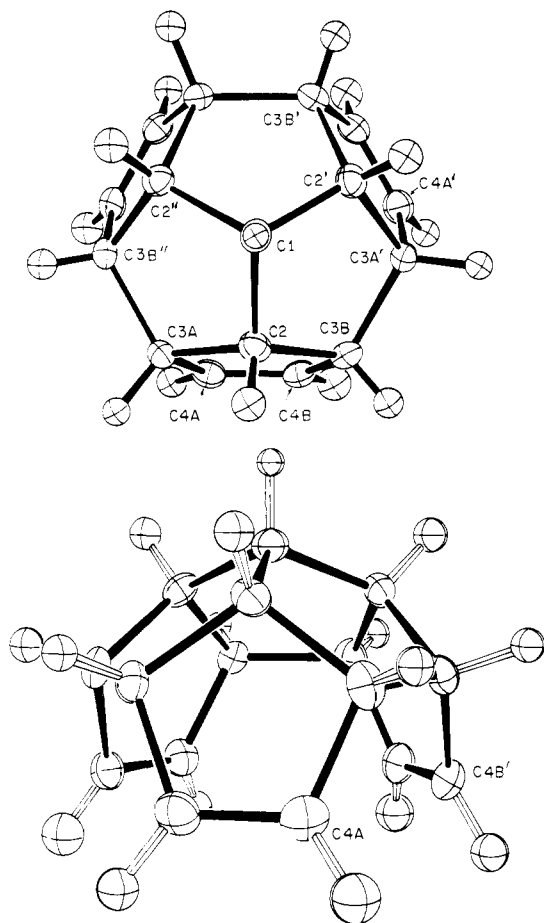
George R. Pettit,\* James J. Einck, John C. Knight  
Cancer Research Institute and Department of Chemistry  
Arizona State University, Tempe, Arizona 85281  
Received June 19, 1978

## Quantitative Assessment of pp- $\sigma$ Overlap in a Topologically Convex Triene. Electronic and Crystal Structure Analysis of C<sub>16</sub>-Hexaquinacene

Sir:

C<sub>16</sub>-Hexaquinacene (**1**) is the third and newest member<sup>1</sup> of a select group of trienes, which includes triquinacene (**2**) and *cis*<sup>3</sup>-1,4,7-cyclononatriene (**3**), whose constituent double bonds adopt an arrangement potentially suitable for effective pp- $\sigma$  overlap.<sup>2</sup> Thus, the question arises as to whether one or more members of this series might partake of neutral homoaromatic character.<sup>3</sup> Photoelectron (PE) spectroscopic investigations of **3**<sup>4</sup> have revealed a sizable interaction between its  $\pi$  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 ( $\beta$ ) of -0.3 eV, a value consistent with the distance (2.46 Å)<sup>5</sup> between the ethylene units. Although the distance in **2** (2.533 Å)<sup>6</sup> is close to that found for **3**, a split of only 0.35-0.4 eV has been found.<sup>7</sup> This difference between **2** and **3** has been explained by hyperconjugative effects.<sup>7,8</sup> Thus, in **3** the interactions of  $\epsilon(\pi)$  and  $a_1(\pi)$  with the  $\sigma$  frame are of similar magnitude, while in



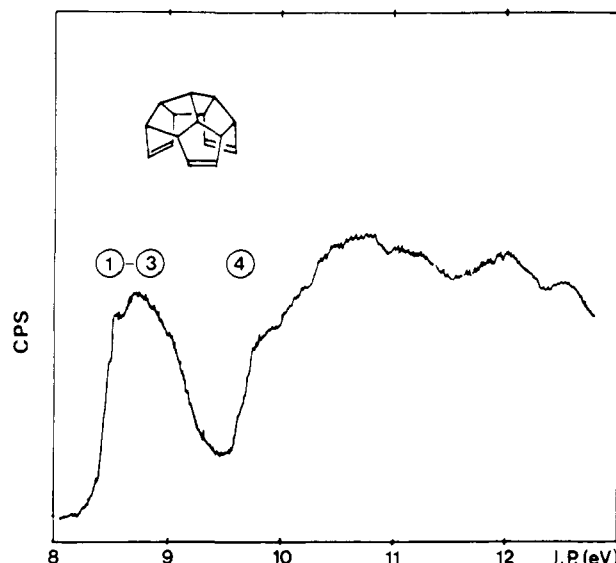


**Figure 1.** Top: view of  $C_{16}$ -hexaquinacene down the threefold axis showing the atomic numbering. Important bond distances and angles follow: C-1-C-2, 1.544 Å; C-2-C-3A, 1.574 Å; C-2-C-3B, 1.542 Å; C-3A-C-3B', 1.561 Å; C-3A-C-4A, 1.505 Å; C-3B-C-4B, 1.513 Å; C-4A-C-4B, 1.323 Å; C-2'-C-1-C-2, 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  $\sigma(\text{C-C}) \approx 0.003$  Å and  $\sigma(\text{C-C-C}) \approx 0.2^\circ$ . 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  $\sigma$  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.<sup>2</sup> 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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.<sup>1</sup> The four carbon resonances (131.57, 60.15, 54.91, and 53.06 ppm) and the attendant  $^{13}\text{C-H}$  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 ( $\epsilon$  20 000), the lack of vibrational fine structure comparing favorably with the electronic spectra given by triquinacene ( $\lambda_{\text{max}}^{\text{isooctane}}$  187 nm ( $\epsilon$  13 000))<sup>9a</sup> and cyclopentene ( $\lambda_{\text{max}}$  180 nm ( $\epsilon$  10 000)).<sup>9b</sup>



**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)° ( $\lambda(\text{Mo K}\alpha) = 0.71069$  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) measurements<sup>10</sup> gave a final data set of 595 unique reflections. Data reduction and weighting were performed in the standard way.<sup>11</sup> The structure, solved by inspection of the Patterson function and refined by conventional Fourier and least-squares techniques,<sup>12</sup> 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  $\text{GOF} = 1.92$ . The final difference Fourier map (average noise level, ca.  $\pm 0.1$   $e^-/\text{\AA}^3$ ) shows no residual electron density  $> 0.30$   $e^-/\text{\AA}^3$ , 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  $10\sigma$ . 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  $5.4^\circ$  dihedral angle with the plane defined by C-3A-C-2-C-3B. For comparison, the same angle in cyclopentene is  $29.0^\circ$ ,<sup>13</sup> and in triquinacene (**2**),  $2.2^\circ$ .<sup>6</sup>

The intramolecular C-4B-C-4A' distance is 2.85 Å, or  $\sim 0.3$  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  $107.0^\circ$ .

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  $\sim 1$  eV from strongly overlapping bands, in a manner very similar to the pattern given by **2**. Because the  $\pi$  units in **1** are

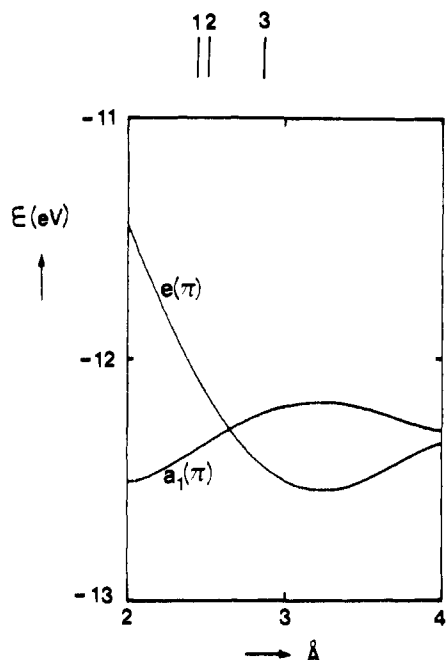


Figure 3. Orbital energy plot showing the variations in  $e(\pi)$  and  $a_1(\pi)$  levels as a function of distance between interacting  $\pi$  bonds.

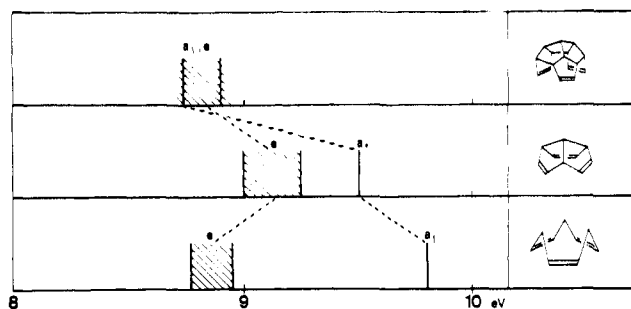


Figure 4. Correlation of the ionization energies of 1-3.

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

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

<sup>a</sup> 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,<sup>14</sup> assuming the validity of Koopmans' theorem.<sup>15</sup>

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  $\pi$  segments. For this purpose, extended Hückel calculations were utilized.<sup>16</sup> 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  $\sigma$  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  $\pi$  bonds, homoconjugation in **1** is completely overridden by hyperconjugation.

The essentially ineffective  $\sigma$  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  $Co(Az)_3$  in a flow-through system.<sup>17</sup>

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

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$$R'' = \left[ \frac{\left( \sum_{hkl} \sum_{j=1}^{n_j} w |F_j^2 - F_{av}^2| \right)}{\left( \sum_{hkl} w (n_j - 1) F_{av}^2 \right)} \right] = 0.049$$
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Gary G. Christoph,\* Jean L. Muthard,<sup>18</sup> Leo A. Paquette\*

Evans Chemical Laboratories  
The Ohio State University  
Columbus, Ohio 43210

Michael C. Böhm, Rolf Gleiter\*

Institut für Organische Chemie  
Technische Hochschule Darmstadt  
D6100 Darmstadt, West Germany

Received June 27, 1978

## Static and Dynamic Stereochemistry of Dicoordinate Phosphorus Cations

Sir:

It has been demonstrated<sup>1,2</sup> that halide ion abstraction from halophosphines results in apparently dicoordinate phosphorus