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In the series of the monocyclic conjugated ketones, called annulunones, the [3], [5] and [7] members or their derivatives have been rather extensively studied. Recently, the [11], [13], [15] and [17] members of the series have been reported. The only missing member is the nine-membered ring ketone, [9]annulenone, the π-electron analog of cyclopentadienone. We wish to report the preparation and properties of the dibenzo derivative of 1, as well as a versatile route to derivatives of the corresponding hydrocarbon 11H-dibenzo[a,c]cyclononatetraene (DBCNT).

Ozonolysis of 2,3-dihydro-1H-cyclopenta[1]phenanthrene (2) yielded the diketone 4, mp 190° (EtOH, 90%); mass spectrum, m/e 250 (M), 222 (M-CO), 194 (M-2CO) and 152 (100%); \( \nu_{\text{CHCl}} \) max \( cm^{-1} \) 1670, 1680 (C=O); \( \lambda_{\text{EtOH}} \) max 230 (ε 16,250) and 285 nm sh (2,200); nmr (CDCl₃) δ = 7.54 ppm (8H, m), 2.56 (4H, m) and 1.9 (2H, m). Treatment of 4 with PhLi in ether afforded 80% of the corresponding diol 5, mp 180° (benzene-hexane); mass spectrum, m/e 406 (M), 388 (M-H₂O) and 370 (M-2H₂O); \( \nu_{\text{CHCl}} \) max \( cm^{-1} \) 3400 (OH); \( \lambda_{\text{EtOH}} \) max 254 (ε 1,250) and 260 nm (1,240). The nmr spectrum shows signals at δ = 8.08 (2H, dd, J = 8.2 Hz assigned to protons

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\begin{align*}
1 & \equiv 2 & X = \text{CH}_2, \ R = \text{H} \\
6 & \equiv 6 & X = \text{CH}_2, \ R = \text{Ph} \\
7 & \equiv \ & X = \text{C}=\text{O}, \ R = \text{Ph} \\
3 & \equiv 3 & X = \text{CH}_2 \\
8 & \equiv 8 & X = \text{C}=\text{O}
\end{align*}
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H₄ and H₅ of the biphenyl system), 7.2 (4H, m H₂, H₃, H₆ and H₇), 7.16 (10H, broad singlet, 6.4 (2H, dd, J = 8.2 Hz, assigned to protons H₁ and H₆ facing the phenyl rings and thus shielded) and 2.15 (8H, m, alicyclic and hydroxyl protons). Dehydration of 5 with p-toluenesulfonic acid in benzene and chromatography on silica-gel afforded 6, a 9,13-diphenyl derivative of DBCNT (2) in 70% yield, mp 113°C (hexane): mass spectrum, m/e 370 (M), 356 (M-CH₂), 278 and 215 (100%); \( \lambda_{\text{max}}^{\text{EtOH}} \) 245 (ε 22,000), 265 (15,400) and 317 nm (90); nmr (CDCl₃) \( \delta = 7.13 \) (18H, m, aromatic), 5.95 (2H, t, H₁₀ and H₁₁, J = 6.0 Hz) and 3.0 (2H, t, allylic H₁₂, J = 6.0 Hz). Dreiding models indicate the molecule of 6 to be nonplanar and dissymmetric, so that the observed equivalence of the allylic protons at room temperature points to a rapid ring inversion.

The synthesis of the dibenzo[9]annulene derivative 7 was achieved by an analogous route starting from 8. Treatment of 8 with ethylene glycol and TsOH gave the ketal, and its ozonolysis gave the triketone monoketal 9, mp 132°C (EtOH, 90%): in the ir the carbonyl absorption appears at 1670 cm⁻¹; \( \lambda_{\text{max}}^{\text{EtOH}} \) 245 (ε 4,800) and 282 nm (800); nmr (CDCl₃) \( \delta = 7.60 \) (8H, m), 3.96 (4H, s, ketal protons) and an AB quartet (\( \delta_A = 3.10, \delta_B = 2.75, \) \( J_{AB} = 14 \) Hz, 4H, assigned to the alicyclic protons). Treatment of 9 with PhLi yields the diol 10, mp 217°C (70%; cyclohexane): \( \lambda_{\text{max}}^{\text{CHCl₃}} \) (cm⁻¹) 3400 (OH), 780, 750 and 700; \( \lambda_{\text{max}}^{\text{EtOH}} \) 257 (ε 4,200) and 325 nm sh (280). The nmr spectrum was similar to that of 5: \( \delta = 8.22 \) (2H, dd, J = 8.2 Hz, assigned to H₄ and H₅), 7.2 (4H, m, H₂, H₇, H₈, H₉), 7.05 (10H, broad singlet, phenyl protons), 6.28 (2H, dd, J = 8.2 Hz), 4.86 (2H, m, OH), 4.1 (4H, s, ketal protons) and an AB quartet (\( \delta_A = 2.91, \delta_B = 2.40 \) ppm, \( J_{AB} = 15.2 \) Hz). Reaction of 10 with p-toluenesulfonic acid afforded the desired 9,13-diphenyl-11H-dibenzo[a,c]cyclononatetraene-11-one (7), mp 193°C (chromatography on silica-gel): mass spectrum, m/e 384 (M), 356 (M-CO), 330, 279 and 254 (100%); \( \lambda_{\text{max}}^{\text{CHCl₃}} \) (cm⁻¹) 1605 (C = O); \( \lambda_{\text{max}}^{\text{EtOH}} \) 229 sh (ε 28,000), 252 (13,300) and 309 nm (18,200). The uv spectrum is in good agreement with the uv spectra of other unsaturated nine-membered ring ketones, but shows higher intensity bands due to the higher degree of conjugation. The nmr spectrum shows signals at \( \delta = 7.30 \) (18H, m), 6.63 ppm (2H, s, vinylic H₁₀ and H₁₁).
The [9]annulenone is a \( 4n+3 \) ring system and could be expected, if planar, to sustain a paramagnetic ring current, which would shift the vinylic protons \( H_{10} \) and \( H_{12} \) to higher field.\(^7\) By comparison with literature data\(^8\) it appears that the vinylic absorption is not shifted and no ring current is present; we could, therefore, assume that the molecule is not planar.\(^9\)
7. a) M. Rabinovitz, A. Gazit and E. D. Bergmann, Chem. Comm. 1430 (1970);  
9. All new compounds gave satisfactory C- and H- analyses.
10. The assignment was confirmed by double irradiation experiments.
11. The ring inversion of cyclononatetraene could not be frozen even at -130°; no change was observed in 2 at -80°. 
12. The uv spectrum of the ketal was typical for a phenanthrene derivative: nmr  
   δ (CDCl₃) = 8.75 (2H, m), 7.75 (6H, m), 4.11 (4H, s, ketal protons) and 3.60 (4H, s, allylic protons); mass spectrum, m/e 276 (M).
13. Variable temperature studies are under way.
15. The [11], [13], [15] and [17] annulenones display a carbonyl absorption at 1600–1630 cm⁻¹. Also tropone derivatives absorb close to this region.
    nonadienone and -trienon derivatives. These compounds absorb in the ir at  
    1610–1620 cm⁻¹ and show high intensity bands in the uv λmax FTOH  283 nm (10,600) and at 227 (14,200), 305 nm (17,200), respectively; their vinylic protons absorb at δ (CDCl₃) = 6.83 and 6.46 respectively.
17. [17]Annulenone was found to sustain such a ring current, while the high field shift of the vinylic protons in [5]annulenone was attributed to other effects. [13]Annulenone has no protons directly attached to the ring, and no effect can be observed.
18. Compound 6 is probably rapidly invertting at room temperature. This point is under investigation.