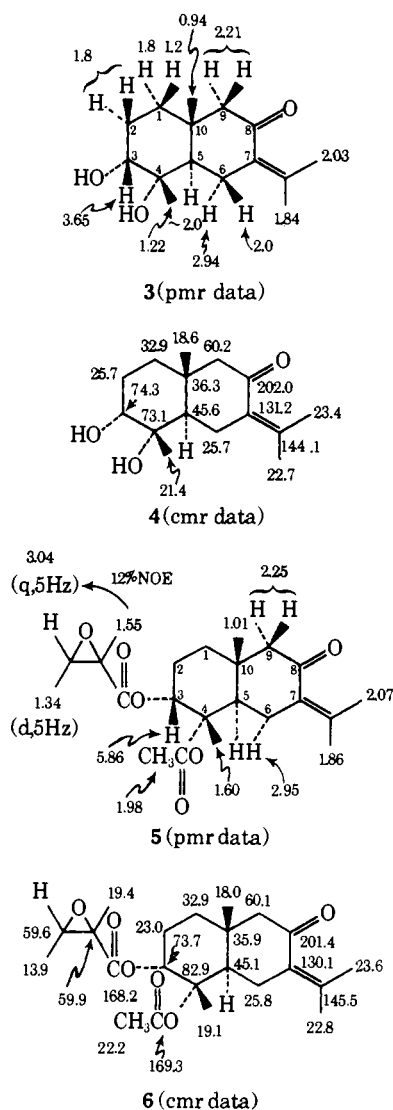


quires this to be adjacent to a quaternary carbon (C-10, and not to C-5) and hence the cisoid enone is linked as shown.



The α -glycol system was proven by consumption of 1 mol of periodate to give the C-3-C-4 cleaved aldehyde ketone with an expected M^+ peak at m/e 250. The α -glycol is cis in view of the ready formation of an acetonide.⁴ Moreover, the fact that the 3-H pmr peak of **1** at 3.65 ppm ($W_{1/2} = 4$ Hz) still retained its narrow half-band width of 4 Hz at 3.94 ppm in the acetonide indicated that the 3-OH and 4-OH are axial and equatorial, respectively, and thus no conformational change had occurred upon acetonide formation; this was corroborated by its CD data, 252 ($\Delta\epsilon -2.50$) and 318 nm ($\Delta\epsilon +1.17$), which were similar to those of cuaehtemone itself.

Originally the *sec*-OH-*t*-OH glycol was considered to be attached to C-2-C-3. This was due to the nmr observation that the 1.8-ppm pmr peaks (a 2 H doublet with $J = 2.5$ Hz overlapping a broad 1 H multiplet) collapsed to a singlet upon decoupling of the 3.65-ppm methine proton. At this point, however, preliminary results of an independent direct X-ray analysis of cuaehtemone showed the glycol was most likely to be

(4) (a) Structure fully supported by spectroscopic data. (b) Compound prepared by the method of J. McCloskey and M. McClelland, *J. Amer. Chem. Soc.*, **87**, 5090 (1965).

attached to C-3 and C-4.⁵ The proton peaks in question, *i.e.*, 1-H and 2-H, in the ester **2** were totally submerged under other signals and thus afforded no information. However, decoupling experiments carried out after addition of $\text{Eu}(\text{fod})_3$ showed the presence of the grouping $^1\text{CH}_2\text{-}^2\text{CH}_2\text{-}^3\text{CH}(\text{O})$ and this now leads to planar structure **1**.⁶

The *cis*-glycol hydroxyls and 10-Me are trans since (i) the 10-Me pmr signal remained unchanged at 0.97 ppm in the 3-monoacetate^{4a} and (ii) only a negligible shift of the 10-Me signal was seen upon $\text{Eu}(\text{dpm})_3$ addition to the diol **1**. In contrast, the Eu reagent caused a large shift in the ~ 1.8 -ppm 1-H⁷ and 2.94-ppm 6-H peaks; these shifts, together with the significantly lower chemical shifts of these protons as compared to their geminal partners (see **3**), are accounted for by a trans ring junction and a 1,3 relation between $3\alpha\text{-OH}(\text{ax})\text{-}1\alpha\text{-H}(\text{ax})$ and between $4\alpha\text{-OH}(\text{eq})\text{-}6\alpha\text{-H}(\text{eq})$.

Flexibility of the enone group prevented application of the various rules proposed for determining the enone chirality,⁸ and hence the following method was employed for determining the absolute configuration. A differential CD curve before and after addition of $\text{Pr}(\text{dpm})_3$ to a CCl_4 solution of the diol showed a negative peak at 317 nm ($\Delta\Delta\epsilon -0.8$), corresponding to a negative chirality between the glycol hydroxyl groups,⁹ and this leads to the absolute configuration shown in **1**.

The ester functions in **2** were shown to be an acetate and a 2,3-epoxy-2-methylbutyrate by pmr. Detection of a 12% NOE on 3'-H upon irradiation of 2'-Me showed the latter ester to be epoxyangelate. As the 3-H signal in **2** is at 5.86 ppm in contrast to the 3-H chemical shift of 4.83 ppm in cuaehtemone 3-monoacetate,^{4a} the epoxyangelate is located at C-3, and this leads to structure **2**.

Acknowledgment. Support from National Institutes of Health Grant No. CA 11572 is gratefully acknowledged.

(5) We are most indebted to Professor W. H. Watson, Jr., Texas Christian University, for this preliminary information. The X-ray studies have since been completed (relative configuration) and will be published elsewhere by Dr. Watson.

(6) The cuaehtemone pmr signals of $^1\text{CH}_2\text{-}^2\text{CH}_2\text{-}^3\text{CH}$ thus constitute a complex proton system which is not amenable to first-order analysis.

(7) The two C-1 methylene protons were found to be in the 1.2- and 1.8-ppm regions since single frequency irradiation around 1.4 ppm, the intermediate position (and a blank region in the pmr), decoupled the 32.9-ppm C-1 cmr signal.

(8) C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, **84**, 870 (1962); W. B. Walley, *Chem. Ind. (London)*, 1024 (1962); R. E. Ballard, S. F. Mason, and G. W. Vane, *Discuss. Faraday Soc.*, No. **35**, 43 (1963); G. Snatzke, *Tetrahedron*, **21**, 439 (1965); A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **93**, 4058 (1971).

(9) K. Nakanishi and J. Dillon, *J. Amer. Chem. Soc.*, **93**, 4058 (1971).

(10) National Institutes of Health Postdoctoral Fellow, 1972-1974.

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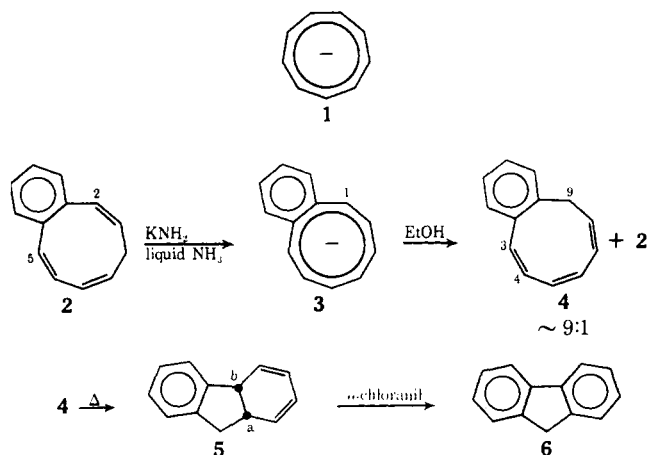
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The Benzocyclononatetraenyl Anion and 1,2-Benzocyclonona-1,3,5,7-tetraene

Sir:

The cyclononatetraenyl anion (**1**) occupies a rather unique position among all-*cis* π -carbomonocycles in

that it is the largest possible member of the series to exist in planar fully delocalized (D_{9h})¹ form and thus to be classed as "aromatic."² Nonetheless, the rather central question of how does this 10π monocycle compare with benzene in terms of π -electron delocalization or will π delocalization in this molecule persist under the perturbation of benzenoid fusion remained largely unanswered, since the obvious model compound necessary for such a study, the benzocyclononatetraenyl anion (**3**), had been unavailable.³ Presently, we describe the generation and direct observation of this substance and, in addition, its use in the preparation of the hitherto unknown benzocyclononatetraene (benzo-CNT) shown in **4**. Treatment of benzo-CNT **2** at



-55° with potassium amide in liquid ammonia, containing trimethylamine as internal standard, produces a dark solution displaying nmr signals⁴ at τ 1.78 (2 H, doublet of doublets, $J = 8$ Hz, 4.5 Hz), 2.18 (2 H, doublet, $J = 14.5$ Hz, H_1) and 2.4–3.5 (7 H, multiplet). Comparison of this spectrum to that of **2**⁵ reveals several structural features of **3**. First, we note that the two 1 H doublets present in the spectrum of **2** (H_2 at τ 3.28 and H_5 at 3.68) reduce to a single 2 H doublet in the spectrum of **3** (H_1 at τ 2.18). This change requires that **3** possess twofold symmetry and hence that the charge formally associated with the C_9 segment of the molecule be delocalized over at least seven of its centers. In fact, brief comparison of the benzenoid resonances of **2** (4 H singlet at τ 2.81)⁵ and **3** (two 2 H doublets of doublets centered at τ 1.78 and 3.04) appears to indicate that charge delocalization in **3** is not limited to the cyclononatetraenyl portion but extends into the benzene moiety as well. Moreover, judging from the significant downfield shift experienced by all protons bound to the C_9 portion of the molecule on going from **2** to **3**,⁶ and

(1) H. E. Simmons, D. B. Chesnut, and E. A. LaLancette, *J. Amer. Chem. Soc.*, **87**, 982 (1965).

(2) For a recent review on the subject, see P. J. Garratt and M. V. Sargent in "Nonbenzenoid Aromatics II," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, Chapter 4.

(3) A dibenzo derivative of **1**, recently prepared, was reported to exhibit nmr characteristics best ascribable to the gradual development of a delocalized π frame: P. J. Garratt and K. A. Knapp, *Chem. Commun.*, 1215 (1970).

(4) We are indebted to Professor S. W. Staley and Mr. A. W. Orvedal for their valuable assistance in the preparation of the nmr sample of **3** and the determination of its spectrum.

(5) A. G. Anastassiou, S. S. Libsch, and R. C. Griffith, *Tetrahedron Lett.*, 3103 (1973).

(6) The downfield shift of signals is especially striking in connection with the two "olefinic" doublets of **2** appearing at τ 3.28 (H_2) and 3.68 (H_5) which merge into a single "aromatic" doublet at τ 2.18 (H_1) on passing to **3**.

this in spite of the shielding effect of the added negative charge, it may safely be concluded that π -electron delocalization in **3** is attended by strong ring diamagnetism.

The nmr characteristics of the benzocyclononatetraenyl anion thus serve to securely classify the molecule as "aromatic" and one best viewed as a 14π unit rather than a benzannelated 10π system. The obvious conclusion then is that the cyclononatetraenyl anion (**1**) closely resembles benzene in its affinity toward π delocalization.

Protonation of **3** provides chemical evidence for its [7.4.0] frame and serves, in addition, as a convenient source of the novel benzo-CNT, **4**. Specifically, slow addition of ethanol to **3** in liquid ammonia at -70° leads to a two-component mixture consisting (nmr) of ca. 90% **4** [nmr (60 MHz, CDCl_3 , -25°) τ 2.85 (4 H, narrow multiplet), 3.28 (1 H, doublet, H_3 , $J_{34} = 11.5$ Hz), 3.76 (1 H, doublet H_4 , $J_{43} = 11.5$ Hz), 4.28 (2 H, narrow multiplet), 4.50 (2 H, narrow multiplet), and 6.43 (2 H, doublet, H_9 , $J \sim 3$ Hz)] and 10% **2** (nmr).^{5,7} Unlike **2**, which is thermally quite stable, isomer **4** is heat sensitive, rapidly ($k_{20.6} = 1.30 \pm 0.12 \times 10^{-4}$ sec⁻¹, $\Delta G^\ddagger = 22.4$ kcal/mol) and cleanly rearranging to benzobicyclic **5** [colorless oil, λ_{max} (C_8H_{14}) 253 nm(sh) (ϵ 2900), 260.5 (3600), 267.5 (4100), 273.5 (3700), and 279(sh) (2000); nmr (60 MHz, CDCl_3) τ 2.79 (4 H, narrow multiplet), 4.20 (4 H, singlet), 6.05 (1 H, broad doublet, $J = 9$ Hz) and 6.6–7.3 (3 H, multiplet); m/e 168 (P^+ ; 86%)]. The structure of **5** follows clearly from the spectral data (the magnitude of J_{ab} (9 Hz) attesting to the presence of cis fusion) and receives added confirmation from its conversion to fluorene (**6**) (mmp, ir, nmr) on exposure to *o*-chloranil.

Finally, we note that the electrocyclicization of **4** to **5**, which is of course permitted by orbital symmetry, does not appreciably differ in rate from that of *cis*⁴-CNT itself ($\Delta G^\ddagger_{20.6} = 22.9$ kcal/mol)⁸ and are thus forced to conclude that benzannelation does not appreciably affect the thermal sensitivity of the CNT frame.

Acknowledgment. We are grateful to the National Science Foundation (GP-38553X) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(7) The proportion in which these two isomers are formed is a sensitive function of the rate of protonation, with increasingly larger quantities of **2** being produced on faster addition of the alcohol. This finding is fully consistent with the lower electron density at C_1 compared to C_3 of the anion indicated by the respective nmr chemical shifts of the protons associated with these positions.

(8) This value was calculated from the activation terms (ΔH^\ddagger and ΔS^\ddagger) given by G. Boche, H. Bohme, and D. Martens, *Angew. Chem.*, **81**, 565 (1969).

(9) National Science Foundation Graduate Trainee 1969–1973.

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¹H, ¹³C, and ¹⁵N Nuclear Magnetic Resonance Studies of a Dinitrogen Complex of Permethyltitanocene. Evidence for Molecular Nitrogen Coordinated "Edge-on" to a Transition Metal

Sir:

In connection with the current interest in transition metal dinitrogen complexes and their possible roles in