a non-hydrogen-bonded enol.[18-20] A 20-fold reduction in acid concentration in $CDCl_3$ causes a change of less than 6 Hz (downfield) in the position of this resonance. The trans-enol **2b** is presumably much less stable and unlikely to be important under these conditions.[22,23] Conformer **2c** is probably not favored since the π-base strength of the carbonyl oxygen exceeds that of the other carboxyl oxygen or enol oxygen, and, further, the carboxyl proton shifts would be moved downfield by this internal hydrogen bond and the enolic proton shifts would presumably be substantially upfield of their observed position. Other conformers lacking an internal hydrogen bond are not likely to be important under equilibrium conditions as has been observed in 3-keto esters.[24] Therefore the enol tautomer is best represented as **2a**. Enol hydroxyl proton shifts do not change from carbon tetrachloride to chloroform-*d*, but these shifts are determined in part by chemical exchange which may serve to obscure small changes in shift.

Separate enol and carboxyl proton resonances were not observed in the more polar solvents. The lack of detectable splitting in the enol methyl and vinyl signals stands in contrast to the observation of a splitting of 0.74 Hz for the analogous protons in methyl acetoacetate.[22]

The broad-band-decoupled ^{13}C NMR spectrum (Table III) of acetoacetic acid in chloroform-*d* is unexceptional, showing the complete keto tautomer spectrum and one peak presumably due to the enol (δ 88.1, olefinic CH carbon). Assignments are in accord with those observed for both methyl[22] and ethyl[14] esters of the acid.

Spectra run at ambient temperatures and at −25 °C in CCl_4 at short intervals immediately upon mixing suggest that acetoacetic acid exists in the keto form in the solid state when crystallized from carbon tetrachloride. This inference appears to be the first comment on the structure of a lower member of this series in the solid state.[25]

Acknowledgment. We thank Jeffrey Bennet for valuable assistance in the preparation of acetoacetic acid. Partial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. Acetoacetic acid, 541-50-4; diketene, 674-82-8; ethyl acetoacetate, 141-97-9; 3-hydroxybut-2-enoic acid, 73018-20-9; ethyl 3-hydroxybut-2-enoic acid, 1522-29-8.

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[18] The potential enediol tautomer from enolization involving the carboxyl group can be excluded from consideration since it is likely to be less stable than the enol derived from the keto function. The lack of detectable enol in malonic acid[19] supports this statement. Further, the enol olefinic CH resonance in the ^{13}C NMR spectrum of acetoacetic acid is within 2 ppm of the analogous resonance in methyl[20] and ethyl[14] acetoacetate enol. If the enediol were present to a significant degree, interconversion with the proposed enol tautomer would occur on a ca. 10^{-16}-s time scale by analogy with related systems[20] and NMR shifts would therefore be a weighted average of the shifts for the two individual tautometers.

[19] Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.; Milwaukee, WI; Vol. 2, No. 150D.

[20] Brown, R. S.; Tse, A.; Nakashima, T.; Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 3157.

[21] The enol hydroxyl proton of methyl acetoacetate in toluene-d_8 appears at δ 12.60.[22]

[22] Matusch, R. *Angew. Chem.* **1975**, *87*, 283.

[23] The trans enol of methyl acetoacetate has been studied by ^1H NMR and was shown to have a methyl proton chemical shift 0.6 ppm downfield of the corresponding peak in the cis isomer (ref 22). We find no unassigned peaks in the expected region of the spectrum.

[24] Veirov, D.; Bercovici, T.; Fischer, E.; Mazur, Y.; Yogev, A. *J. Am. Chem. Soc.* **1977**, *99*, 2723 and references therein.

[25] A previous report lists X-ray crystal spacings for the C_8–C_{24} homologues of acetoacetic acid.[26]

[26] E. Stenhage *Ark. Kemi* **1957**, *3*, 381.

Cycloocta[*def*]fluorene: A Planar Cyclooctatetraene Derivative.[1] Paratropicity of Hydrocarbon and Anion

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The synthesis of cycloocta[*def*]fluorene (**1**) from cyclopenta[*def*]phenanthrene (**5**) is described. Hydrocarbon **1** shows paratropic antiaromatic character as deduced from the ^1H NMR spectra and its low acidity ($pK_a = 27$). The antiaromatic character of **1** is attributed to the presence of a planar cyclooctatetraene (COT) moiety. The deprotonation and the formation of cycloocta[*def*]fluorenyl anion (**13**) are presented. The anion **13** exhibits paratropic character which may originate in peripheral delocalization of 16 π electrons.

The thermodynamic characteristics of conjugated molecules are the basis for the concepts of aromaticity and antiaromaticity.[3] While aromaticity ascribes enhanced stabilization of cyclic delocalized molecules relative to their respective acyclic systems, antiaromaticity infers the

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[1] For preliminary reports, see: (a) Willner, I.; Gutman, L. A.; Rabinovitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 4167. (b) Willner, I.; Rabinovitz, M. *Tetrahedron Lett.* **1976**, 1223.

[2] (a) Taken in part from the Ph.D. Thesis of I. Willner. (b) To whom correspondence should be addressed.

[3] For general reviews, see: *Chem. Soc. Spec. Publ.* **1967**, *No. 21*. Bergmann, E. D., Pullman, B., Eds.; "Aromaticity, Pseudoaromaticity, Antiaromaticity"; Jerusalem Academic Press: Jerusalem, 1971. Garratt, P. J. "Aromaticity"; McGraw-Hill: London, 1971. Agranat, I. "MTP International Review of Science"; Butterworths: London, 1973; Vol. 3, Chapters 5 and 8; 1976, Vol. 3, Chapter 11. Breslow, R. *Chem. Eng. News* **1965**, *43*, 90; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 565.

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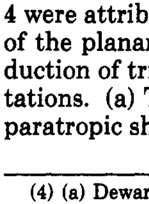
unique destabilization of a delocalized cyclic system relative to its acyclic counterpart.[4] In recent years theoretical and experimental efforts have been directed toward the study of the Hückeloid-aromatic and antiaromatic series $(4n + 2)$-π- and $4n$-π-electron systems, respectively.

The prevalence of induced ring currents in conjugated molecules led to the establishment of experimental criteria for determination of aromatic and antiaromatic properties (diatropicity and paratropicity, respectively).[5,6] The induced diamagnetic ring current serves as an efficient probe for the characterization of the aromatic series. However, in the antiaromatic series, the paratropic effect is known to be a weak one[6] on both theoretical and experimental grounds. The links between antiaromaticity and aromaticity can be examined in the $4n$-π-conjugated series. The *planar* $4n$-π series would be expected to exhibit both antiaromatic paratropic properties and a dual character in attaining aromaticity.[7] Cyclobutadiene is unstable and can be captured only in a matrix, thus preventing detection of its supposedly paratropic character.[8] Moreover, the higher homologues of this series, e.g., cyclooctatetraene (COT), [12]annulene, and [16]annulene, are nonplanar, and therefore it has been impossible to detect the paratropicity expected.[9] We present a study of a polycyclic system bearing an 8-π cyclooctatetraene component and describe its properties.

Results and Discussion

Cycloocta[*def*]fluorene (1), a Planar Paratropic Antiaromatic System. In order to form planar molecules from otherwise nonplanar [4*n*]annulenes, triple bonds can be introduced into their ring frameworks. Accordingly, it has been claimed that [12]- and [16]dehydroannulenes exhibit paratropicity.[9] In order to flatten the tub conformation of cyclooctatetraene (COT), Sondheimer[10] prepared dibenzocyclooctadiene-3,7-diyne (**3**), dibenzocyclooctatrien-7-yne (**2**), and benzocyclooctatriene-3,7-diyne (**4**).



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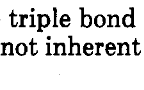

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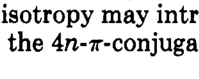

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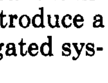
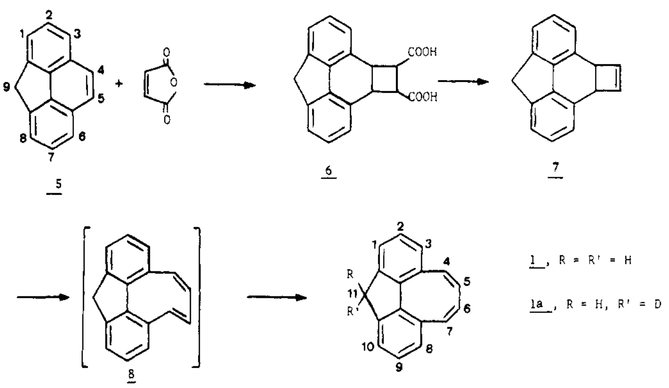


4

As **3** was known to be planar[11] from X-ray studies, the relatively high-field shifts of the vinylic protons in **2** and **4** were attributed to paratropic character, a consequence of the planar cyclooctatetraene component. The introduction of triple bonds suffers from two significant limitations. (a) The triple bond anisotropy may introduce a paratropic shift not inherent in the $4n$-π-conjugated system; e.g., **4**[12] shows enhanced paratropicity relative to **2** which may originate from the effect of the two triple bonds upon the shift of the vinylic protons.[13] (b) The number of proton sites which may serve as paratropicity probes is reduced.

Scheme I



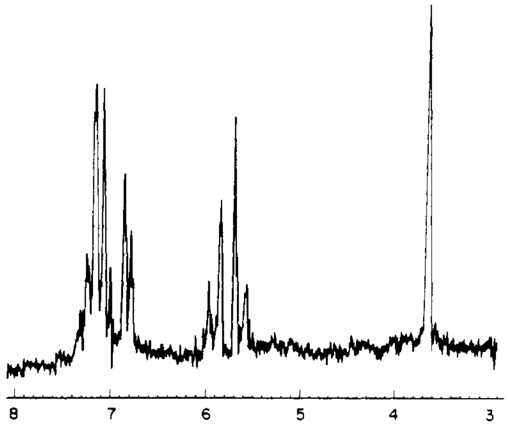


Figure 1. Proton spectrum (100 MHz, $SiMe_4$ internal reference) of cycloocta[*def*]fluorene (**1**).

The approach[1] to examination of the paratropic character of the cyclooctatetraene system was based on designing a rigid polycyclic system including a planar COT moiety. Cycloocta[*def*]fluorene (**1**) was the system of choice. A closely related system, i.e., cycloocta[*def*]biphenylene (**12**), was prepared by Wilcox.[14] The molecular architecture of **1** represents a fusion of the rigid planar fluorene to a butadiene bridge. The complementary angles at fluorene positions 4a and 5a, as determined by X-ray crystallography (132°), are close to that of a planar octagonal angle (134°). The rigidity of the polycyclic system should force the COT component into planarity, thus permitting examination of the system's paratropic antiaromatic properties.

Cycloocta[*def*]fluorene (**1**) was prepared as outlined in Scheme I. Cyclopenta[*def*]phenanthrene (**5**) was reacted in a [2 + 2] photochemical cycloaddition[15] with maleic anhydride to form, after hydrolysis, the respective diacid **6**. In the mass spectrum the expected molecular ion (M^+, *m*/*e* 306) underwent successive fragmentations of water, carbon dioxide, carbon monoxide, and acetylene (*m*/*e* 288,

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[4] (a) Dewar, M. J. S. "The Molecular Orbital Theory for Organic Chemistry"; Wiley: New York, 1961. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3345.

[5] (a) Elvidge, J. A. *Chem. Commun.* **1965**, 43. (b) Hall, G. G.; Hardisson, A.; Jackmann, L. M. *Tetrahedron Suppl.* **1963**, *19*, 2, 101.

[6] (a) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811. (b) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111. (c) Nakajima, T.; Kohola, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 804.

[7] The two-electron oxidation and reduction of dibenzo[*b*,*f*]pentalenes was recently reported. (a) Willner, I.; Rabinovitz, M. *J. Am. Chem. Soc.* **1978**, *100*, 337. (b) Willner, I.; Becker, J. Y.; Rabinovitz, M. *Ibid.*, in press.

[8] (a) Maier, G. *Angew. Chem.* **1974**, *86*, 491; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425. (b) Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261.

[9] Untch, K. G.; Wysocki, D. C. *J. Am. Chem. Soc.* **1966**, *88*, 2608. (b) Sondheimer F.; Wolovski, R.; Garratt, P. J.; Calder, I. C. *Ibid.* **1966**, *88*, 2610.

[10] Wong, H. N.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1974**, *96*, 5604.

[11] Destro, R.; Pilati, T.; Simonetta, M. *J. Am. Chem. Soc.* **1975**, *97*, 5604.

[12] Wong, H. N. C.; Sondheimer, F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 117.

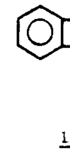
[13] Staab, H. A.; Graf, F. *Chem. Ber.* **1970**, *103*, 1107.

[14] (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914. (b) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889. (c) Wilcox, C. F., Jr.; Uetrecht, J. P., Grohmann, K. G. *J. Am. Chem. Soc.* **1972**, *94*, 2532.

[15] A similar reaction has been carried out on phenanthrene: Vogel, E.; Frass, W.; Wolpers, J. *Angew. Chem.* **1963**, *75*, 979.

212, and 190). This evidence supports the polycyclic structure containing a fused cyclobutane ring with two adjacent carboxylic groups. Didecarboxylation of **6** either by lead tetraacetate[16] or by electrochemical means,[17,18] afforded **7**. The molecular ion (*m/e* 216) underwent a fragmentation of acetylene (*m/e* 190). This supports the presence of a fused cyclobutene ring characterized by its easy fragmentation. Application of Paquette's oxidative didecarboxylation[19] using copper salts in quinoline afforded cyclopenta[*def*]phenanthrene (**5**). The formation of **5** is rationalized by the intermediate formation of **7** which undergoes cycloreversion to form **5** and acetylene, thus emphasizing the lability of this bicyclic skeleton. Thermolysis of **7** at 400 °C afforded a mixture of cyclopenta[*def*]phenanthrene (**5**, 14%) and cycloocta[*def*]fluorene (**1**, 84%). The formation of **5** is a result of cycloreversion which competes with the thermal isomerization to **1**. The structure of **1** was fully established by its ^{1}H NMR spectrum (Figure 1), which consisted of an aromatic multiplet at 6.83–7.80 ppm, an A_2B_2 pattern assigned to the vinylic protons H_4–H_7, and a singlet at 3.63 ppm assigned to the protons at position 11. The vinylic A_2B_2 spectrum consists of a double doublet at 5.90 ppm attributed to H_4 and H_7 and a double doublet at 5.68 ppm attributed to protons H_5 and H_6. The observation that the vinylic protons appear as a single AB pattern and its vicinal coupling constants (J = 10 Hz) established a cis,cis configuration of the double bonds in the COT component of **12**. The thermal isomerization of **7** is expected to occur in a conrotatory fashion to form cis,trans structure **8**.[20-22] However, the formation of a cis,cis configuration can be rationalized by the initial conrotatory isomerization of **7** into **8** which then undergoes a thermal double bond isomerization into *cis,cis*-cycloocta[*def*]fluorene (**1**).[22] No isomerization occurred when the thermolysis was conducted at lower temperatures in an attempt to trap the initial product **8**.

In order to relate paratropic character to cycloocta[*def*]fluorene (**1**), a nonplanar system closely related in structure is required. Dibenzo[*a,c*]cyclooctatetraene (**9**)



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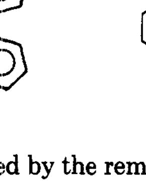
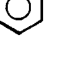


9



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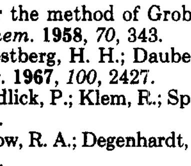
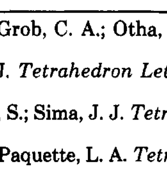


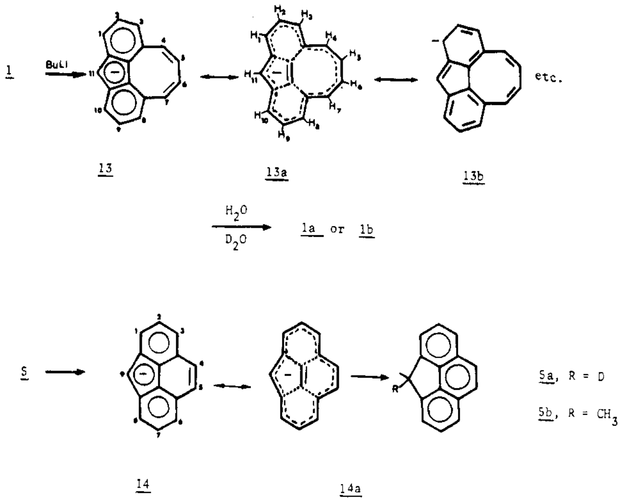
11



12

is schematically formed by the removal of the "methylene bridge" from **1**. In this system, the ortho biphenyl interactions operate to force the system into a nonplanar structure, as recently discussed by Gunther.[23] Dibenzo[*a,c*]cyclooctatetraene[15] was synthesized as described above by starting with phenanthrene. The ^{1}H NMR spectrum of **9** consists of an aromatic multiplet at 7.2 ppm, and the vinylic protons appear as an A_2B_2 pattern (δ_A 6.82, δ_B 6.32, J = 11 Hz). Comparison of the vinylic proton chemical shifts of **1** with those of **9** indicates paramagnetic shifts of H_4, H_7 and H_5, H_6 relative to the respective protons of **9** (H_A and H_B). This paratropic shift implies a planar structure of the COT component of **1** and supports the initially suggested strategy aimed at the achievement of this challenge. Similarly, a comparison of the vinylic proton chemical shifts of **1** and the closely related planar system **12** to other polycyclic cyclooctatetraenes, e.g., **10** and **11**, also shows that the vinylic protons of cycloocta[*def*]fluorene show significant paratropic shift.[14,24] Unfortunately, hydrocarbon **1** is isolated as an oil, and a X-ray structure determination could not be accomplished. Further support for the planar structure of **1** comes from the comparison of its UV spectrum with that of **9**. While **9** shows typical biphenyl absorption and a styrene chromophore, **1** shows an additional band (λ = 346 nm) due to a forbidden transition (ϵ 1360). This transition is characteristic of planar $4n$-π-conjugated systems and requires minimal excitation energy.[25]

Scheme II



Cycloocta[*def*]fluorenyl Anion 13, a Peripheral 16-π Antiaromatic System. The planar structure of cycloocta[*def*]fluorene (**1**) prompted us to study the events encountered in its deprotonation.[1] The fact that **1** includes a fluorene component may, after its deprotonation, indicate an anion composed of an aromatic fluorenyl anion and an antiaromatic planar cyclooctatetraene moiety. On the other hand, if the anionic charge is delocalized over the entire framework, it will result in a peripheral 16-π-electron system perturbed by an ethylene bridge. Thus, from a peripheral aspect, cycloocta[*def*]fluorenyl anion **13a** would behave as a perturbed [15]annulenyl anion, **13b** (Scheme II). These two aspects seem to be fundamental in the understanding of the $4n$-π-conjugated antiaromatic systems.

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(16) For the method of Grob, cf.: Grob, C. A.; Otha, M.; Weiss, A. *Angew. Chem.* **1958**, *70*, 343.

(17) Westberg, H. H.; Dauben, H. J. *Tetrahedron Lett.* **1968**, 5117; *Chem. Ber.* **1967**, *100*, 2427.

(18) Radlick, P.; Klem, R.; Spurlock, S.; Sima, J. J. *Tetrahedron Lett.* **1968**, 5117.

(19) Snow, R. A.; Degenhardt, C. R.; Paquette, L. A. *Tetrahedron Lett.* **1976**, 4447.

(20) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(21) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781; *Science* **1970**, *167*, 825.

(22) Willner, I.; Rabinovitz, M. *Tetrahedron Lett.* **1976**, 3335.

(23) Gunther, H.; Shyonkh, A.; Cremer, D.; Frisch, K. H. *Justus Liebigs Ann. Chem.* **1978**, 150. Gunther, H.; Gunther, M. E.; Mondeshka, D.; Schmickler, H. *Ibid.* **1978**, 165.

(24) (a) Garratt, P. J.; Mitchell, R. H. *Chem. Commun.* **1968**, 719. (b) Kaplan, F. A.; Roberts, B. W. *J. Am. Chem. Soc.* **1977**, *99*, 518.

(25) (a) Wirz, J. *Helv. Chim. Acta*, in press. (b) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Wiley: New York, 1963.

Table I. ^1H NMR Data (δ) of Cycloocta[*def*]fluorene (1) and Cycloocta[*def*]fluorenyl Anion 13

	H_1, H_3, H_8, H_{10}[b]	H_2, H_9[b]	H_4, H_7[b]	H_5, H_6[b]
1	7.4[a]	7.4[a]	5.90	5.68
13	7.08 (d, J = 8 Hz)	6.38 (t, J = 8 Hz)	5.42 (dd, J_1 = 10 Hz, J_2 = 4 Hz)	4.96 (dd, J_1 = 10 Hz, J_2 = 4 Hz)

[a] Average value, center of multiplet. [b] $\Delta\delta_i = \delta_i(1) - \delta_i(13)$. For H_1, H_3, H_8, and H_{10} $\Delta\delta_i = -0.3$ ppm. For H_2 and H_9 $\Delta\delta_i = -1$ ppm. For H_4 and H_7 $\Delta\delta_i = -0.5$ ppm. For H_5 and H_6 $\Delta\delta_i = -0.7$ ppm.

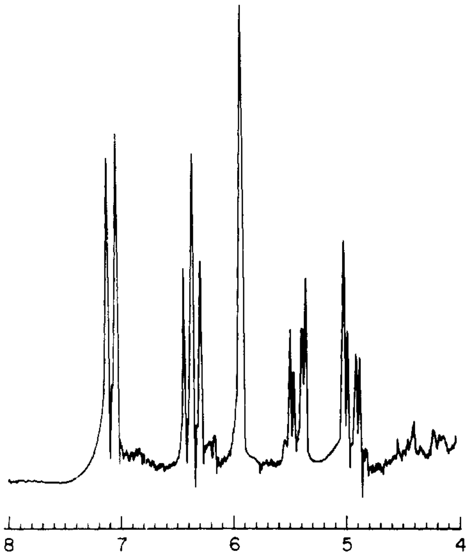

Figure 2. Proton spectrum (THF-d_8, 100 MHz, $SiMe_4$ internal reference) of cycloocta[*def*]fluorenyl anion 13.

Treatment of 1 with *n*-butyllithium in THF-d_8 resulted in a dark red solution attributed to cycloocta[*def*]fluorenyl anion **13**. Quenching of the anion with D_2O afforded 11-deuteriocycloocta[*def*]fluorene (**1a**). The ^1H NMR spectrum of **13** (Figure 2) consists of a doublet at 7.08 ppm assigned to protons H_1, H_3, H_8, and H_{10}, a triplet at 6.38 ppm assigned to protons H_2 and H_9, and an A_2B_2 pattern which consists of a double doublet at 5.42 ppm (H_4, H_7) and a double doublet at 4.96 ppm (H_5, H_6). Proton H_{11} is observed at 5.83 ppm (singlet). Table I summarizes the change in the chemical shifts of the vinylic and benzo protons accompanying the deprotonation process. It can be seen that all protons are shifted to high field (Δ_{total} = 5.6 ppm). This upfield shift can originate both from the shielding due to the negative charge and from a paratropic antiaromatic contribution as a result of the formation of the peripheral 16-π-conjugated system **13a**. The observation that the vinylic protons H_4–H_7, which are remote from the deprotonation site, are shifted paramagnetically to the highest extent rules out an exclusive inductive shielding mechanism. Furthermore, a resonance shielding effect of the negative charge would cause amplification of the negative charge at positions 1 and 3 (and 8 and 10) due to the contributions of **13b** etc. The NMR spectrum of **13** reveals a different phenomenon; namely, protons H_2 and H_9 show the most extensive paratropic shift. It seems, therefore, that shielding effects are not the sole explanation for the upfield shifts observed.

In order to better understand the effect of the induced paramagnetic ring current vs. charge shielding, we studied the deprotonation of cyclopenta[*def*]phenanthrene (**5**). Formally, **5** can be visualized as **1** shortened by one C=C bond. Cyclopenta[*def*]phenanthrenyl anion (**14**) includes 14 π electrons in a conjugated system and may be represented as a peripheral [13]annulenyl anion perturbed by an ethylene bridge, e.g., **14a**. The chemical shifts of protons H_4 and H_5 in **14** represent the influence of the shielding due to the negative charge on a remote double bond in a polycyclic aromatic system. Anion **14** was prepared by the deprotonation of **5** with *n*-butyllithium in THF-d_8. Quenching of **14** with D_2O or methyl iodide afforded the electrophilic substitution products, viz., **5a** and **5b**. The ^1H NMR spectrum of **14** consists of a singlet at 7.73 ppm (H_4, H_5), a multiplet centered at 7.41 ppm (H_2, H_3, H_6, H_7), a double doublet at 7.05 ppm (H_1, H_8), and a singlet at 6.06 ppm assigned to H_9. The proton resonances of **14** show a downfield shift compared with those of the hydrocarbon **5** (total downfield shift of 2.0 ppm). The observed diamagnetic shifts despite the shielding of the negative charge are attributed to the formation of an aromatic diatropic polycyclic anion and are rationalized by the formation of a perturbed peripheral [13]annulenyl anionic system, **14a**. Furthermore, protons H_4 and H_5 in **14** are shifted diamagnetically to the highest extent. Thus, the negative charge shielding on the "vinylic bond" protons remote from the site of the deprotonation is relatively weak. Earlier in this paper the aromaticity and antiaromaticity of conjugated systems were verified on the basis of paratropic or diatropic shifts in the ^1H NMR spectra. However, from a theoretical point of view the terms aromaticity or antiaromaticity reflect an electronic stabilization or destabilization as calculated by MO calculations.[26] Hence an interrelation between the experimental criteria and the theoretical definition must exist. Indeed, it has been shown that the induced magnetic field in a cyclic conjugated molecule can be described as a sum of diamagnetic and paramagnetic contributions of electron densities in the ground and excited states. The electron density of the ground state will contribute to a diamagnetic component while excited-state electron densities contribute to a paramagnetic component. Since 4n-π-conjugated systems are characterized by a small HOMO–LUMO separation, the paramagnetic component, as a result of significant excited-state electron densities, should be emphasized. Therefore, the application of experimental paratropic effects is justified also from a theoretical point of view.

The limited charge shielding on protons H_4 and H_5 in **14** supports the hypothesis that the upfield shifts observed in cycloocta[*def*]fluorenyl anion **13** do not originate only from charge-shielding effects. The paratropicity of **13** is attributable to its antiaromatic character due to peripheral delocalization of 16 π electrons. Thus, cycloocta[*def*]fluorenyl anion **13** represents a [15]annulenyl antiaromatic paratropic system perturbed by a vinylic bond, viz., **13b**. It should be noted that the assignment of paratropic antiaromatic character to **13** is based on relatively small values of paratropic shifts. Since on a theoretical basis[26] the paratropic shift should be small, our observations are reasonable.

So far, the antiaromaticity attributed to the cycloocta[*def*]fluorenyl anion (**13**) was based on its ^1H NMR spectrum. However, the antiaromaticity should also be reflected in its acidity.[27] The high acidity of fluorene (pK_a

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[26] (a) Bockelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695. (b) Phillips, J. B.; Molyneux, R. I.; Sturm, E.; Bockelheide, V. *Ibid.* **1967**, *89*, 1704. (c) Pople, J. A. *J. Chem. Phys.* **1964**, *41*, 2559. (d) Ferguson, A. F.; Pople, J. A. *Ibid.* **1965**, *42*, 1560.

= 22.4) is attributed to the thermodynamic stability of the aromatic conjugate base, the fluorenyl anion. Therefore, the antiaromaticity of **13** should manifest itself in the relatively low acidity of its fluorene component. In other words, the decreased acidity of cycloocta[*def*]fluorene (**1**) relative to other fluorene derivatives should provide additional proof of the antiaromatic character of its anion. On the basis of the variation in the chemical shifts of protons attached to the deprotonation site, Schaeffer[28] has reported an empirical method for determining the pK_a values of hydrocarbons (eq 1), where Δ = [proton chemical

$$\mathrm{p}K_a = 3.20\Delta + 35.12 \qquad (1)$$

shifts (ppm) of the protons attached to the deprotonation site (δ_{AH})] − [proton chemical shifts (ppm) of the proton at the same site on the anion (δ_{A^-})]. Substitution of the respective values of **1** and **13** in eq 1 affords an empirical pK_a = 28 for **1**. Similar treatment of the couple cyclopenta[*def*]phenanthrene (**5**) and its conjugate base gives a value of pK_a = 26.8 for **5**. Thus, the predicted pK_a value of **1** represents a low acidity relative to other fluorene derivatives.[29] Experimentally, the pK_a value of **1**, i.e., [A_1H], can be determined by equilibration with cyclopenta[*def*]phenanthrenyl anion (**14**) ([A_2^-], eq 2a and 2b).[30]

$$A_1H + A_2^- \rightleftharpoons A_1^- + A_2H \qquad (2a)$$

$$\mathrm{p}K_{a_1} - \mathrm{p}K_{a_2} = \log\,[A_2^-]/[A_2H] - \log\,[A_1^-]/[A_1H] \qquad (2b)$$

Setting the respective values in eq 2b afforded a pK_a of 27.8 for cycloocta[*def*]fluorene (**1**). The ^{1}H NMR spectrum of **1** as discussed above reveals that the molecule bears a C_{2v} symmetry (protons H_{11} and $H_{11'}$ appear to be equivalent). Hence, these symmetry properties imply that the fluorene component in **1** is in a planar structure, similar to the fluorene component of **5**. As a result, the low acidity of **1** does not originate from structural changes at the deprotonation site. It should, however, be noted that the acidity of a hydrocarbon is not directly related to aromaticity or antiaromaticity. The acidity of a hydrocarbon is a function of the stability of the conjugate base formed in dissociation toward reassociation to the parent hydrocarbon. Thus, indirectly, the comparison of the acidities of two hydrocarbons bearing similar acidic sites will reflect the stability of the respective anions. Since the parent hydrocarbons **1** and **5** have similar structural properties (C_{2v} symmetry) the acidic sp^3 functions also have similar structural properties. Thus, the difference in acidity of **1** and **5** reflects the different stabilities of the respective conjugate bases **13** and **14**. This difference can be attributed to electronic destabilization of **13** due to antiaromatic character. It should be noted that the acidity value of **1** is the lowest known for hydrocarbons in the fluorene series.[30]

Streitwieser has shown that the acidity of conjugated hydrocarbons is directly proportional to the difference between the π energies of the anionic system (A^-) and the parent hydrocarbon (AH)[31] (eq 3). In this equation a high

$$\Delta E_\pi = (E_\pi)_{A^-} - (E_\pi)_{AH} = 2\alpha + \Delta M\beta \qquad (3)$$

ΔM value represents a high acidity for the hydrocarbon. Our HMO calculations showed ΔM values of 1.58 and 1.2 for cyclopenta[*def*]phenanthrene (**5**) and cycloocta[*def*]fluorene (**1**), respectively. According to Streitwieser's correlation[31] these ΔM values represent pK_a values of 25 and 28 for **5** and **1**, respectively. Very recently, Trinajstic[32,33] reported a method based on graph theory for the calculation of the resonance energy per electron according to the system's topology (TRE-PE). Applying this calculation to cycloocta[*def*]fluorenyl anion **13**, one obtains a negative value of resonance energy per electron (−0.011β), further emphasizing the antiaromatic character of this anion. These results stress the antiaromatic character of the cycloocta[*def*]fluorenyl anion **13**. The peripheral representation of **13** as a perturbed [15]annulenyl anion, viz., **13b**, accounts for the unique antiaromatic characteristics of the system.

Experimental Section

General Methods. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 137 and Model 337 spectrometers. Ultraviolet spectra were recorded with the aid of a Unicam SP-820 spectrometer. Mass spectra were determined on Varian MAT Model 311 and 111 instruments. Column chromatography was carried out on 4-cm-diameter columns. The absorbents were silica gel (70–325 mesh) or aluminium oxide S (neutral, active, 70–290 mesh). Preparative chromatography was carried out on 2.0-mm plates of silica SIL G-200 UV$_{254}$ (Machery Nagel). All solvents were redistilled prior to chromatography. The usual workup procedure was carried out as follows. The reaction mixture was extracted with dichloromethane. The organic layer was then washed with dilute acid, base, and water, dried over magnesium sulfate, filtered, and evaporated. NMR chemical shifts are reported in parts per million downfield from Me$_4$Si (δ). The proton spectra were recorded on a Varian HA-100D spectrometer at 100 MHz. The assignments were assisted by double-resonance experiments carried out with the aid of a Hewlett-Packard 4204A oscillator. The assignments were assisted with off-resonance experiments.

1,2:3,4-Fluorenobicyclo[4.2.0]octadiene-5,6-dicarboxylate (6). In a 1-L irradiation flask equipped with a magnetic stirrer and a reflux condenser were introduced 5 g (25 mmol) of cyclopenta[*def*]phenanthrene (**5**, Fluka AG), 2.7 g (25 mmol) of powdered maleic anhydride, 400 mg of benzil (sensitizer), and 750 mL of dry purified hexane. Nitrogen gas was bubbled into the solution throughout the irradiation. The solution was stirred and irradiated for 5 h with an external 450-W Hanovia mercury lamp. A yellow solid starts to precipitate after 1 h. After 5 h the solid was filtered, introduced into 45 mL of aqueous 1.46 M KOH, and refluxed for 10 min. The aqueous solution was then acidified (pH 3) with 10% HCl, and the white crystalline solid was left overnight, filtered, and dried (KOH). The yield is 5.3 g (68%) of the diacid **6**: mp 184 °C (acetone–petroleum ether); IR (Nujol) 3300 (br), 1710, 1380, 1250, 770, 720 cm^{-1}; mass spectrum, *m/e* (relative intensity), 307, 306 (m, 6), 289, 288 (M − H$_2$O), 246, 215, 191, 190 (100), 189. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.57. Found: C, 74.3; H, 4.5.

1,2:3,4-Fluorenobicyclo[4.2.0]octatriene (7). A. Decarboxylation with Lead Tetraacetate.[16] To a three-necked flask equipped with a magnetic stirrer and protected from moisture were introduced under N$_2$ 1.25 g (4.1 mmol) of diacid **6**, 40 mL of dry benzene, and 1.1 mL of dry pyridine. The mixture was heated to 50 °C, and 4.2 g (9.2 mmol) of lead tetraacetate was added. When the gas evolution ceased, the reaction mixture was refluxed for an additional 2 h, cooled, and poured onto 300 mL of dilute (5%) nitric acid. The brown oil obtained after the usual workup was chromatographed on 100 g of Florisil and eluted with benzene. The elution afforded 210 mg of **7**: 21%; mp 98 °C (EtOH). In the presence of oxygen, under similar conditions, the yield was 5%: IR (KBr) 3030, 2930, 2900, 1630, 1455, 1430, 1265, 1090, 800, 780, 745, 705 cm^{-1}; UV (cyclohexane) 244 nm (ε 18000), 231 (16200), 238 (12200), 254 (10800), 263 (sh, 10400), 276

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[27] (a) Jones, J. R. *Q. Rev., Chem. Soc.* 1971, *25*, 365. (b) Fischer, H.; Rewicky, P. *Prog. Org. Chem.* 1968, *7*, 116.

[28] Schaeffer, D. J. *Chem. Commun.* 1970, 1043.

[29] Streitwieser, A.; Hollyhead, W. B.; Pudjaatmaka, A. H.; Owens, P. H.; Kruger, T. L.; Rubenstein, P. A.; MacQuarrie, R. A.; Brokaw, M. L.; Chu, W. K. C.; Niemeyer, H. M. *J. Am. Chem. Soc.* 1971, *93*, 5088.

[30] Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter 1.

[31] Streitwieser, A. *Tetrahedron Lett.* 1960, 23.

[32] Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* 1977, *99*, 1692. See also: *Croat. Chem. Acta* 1976, *48*, 87.

[33] Randic, M. *J. Am. Chem. Soc.* 1977, *99*, 445.

(11 500), 284 (9300), 300 (sh, 3000); mass spectrum, *m/e* (relative intensity) 217, 216 (100), 215, 213, 191, 190 (88), 189; ^{1}H NMR ($CDCl_3$) 7.12–7.77 (m, 6 H), 6.10 (s, 2 H), 4.44 (s, 2 HO), 3.84 ppm (s, 2 H). Anal. Calcd for C and H: C, 94.44; H, 5.55. Found: C, 93.9; H, 5.7.

B. Electrochemical Decarboxylation.[17] The diacid was placed in a cooled electrolysis cell equipped with a reflux condenser and a magnetic stirrer. The electrolysis was carried out on 2.5 g of **6** (11.4 mmol) in 90 mL of pyridine–water (80:20) and 1.9 mL of triethylamine during 4 h at 100 V and 0.6–0.8 A. The mixture was poured onto 400 mL of 10% HCl, worked up in the usual manner, and chromatographed on 80 g of silica gel. Elution with benzene afforded 350 mg (20%) of a product identical with that described above.

Thermal Rearrangement of 7. Preparation of Cycloocta[*def*]fluorene (1). The following thermolysis apparatus was constructed for this experiment. In an horizontal pyrolysis oven was placed a glass tube (90 cm in length and 1.5 cm in diameter) filled with glass chips (1–2 mm) and equipped with a capillary inlet, a nitrogen gas inlet, and an efficiently cooled (–78 °C) outlet. The solution of the compound to be pyrolyzed was injected with a syringe into the inlet with an adjustable motor-driven system at a fixed rate. The oven was heated to 400 °C for 45 min and flushed with nitrogen. A solution of 200 mg of **7** (0.9 mmol) in 1.2 mL of benzene was introduced into the oven at a rate of 1 mL/min. The system was washed with dichloromethane, and the mixture was filtered, evaporated, and chromatographed on 110 g of Florisil. The column was eluted with benzene–hexane (1:1). In the first fraction (50 mL) 26 mg of 4,5-methylenephenanthrene (**5**) was recovered, and in the second fraction 165 mg (84%) of cycloocta[*def*]fluorene (**1**) (red oil) was obtained: IR (neat) 3060, 3020, 2930, 1425, 1400, 1160, 820, 770, 730, 680 cm^{-1}; UV (cyclohexane) 253 nm (ϵ 29 500), 273 (sh, 21 200), 300 (4600), 246 (sh, 1360); mass spectrum, *m/e* (relative intensity) 216 (M, 100), 215, 191, 190, 189, 187; ^{1}H NMR ($CDCl_3$) 6.83–7.80 (m, 6 H), 5.90 (dd, 2 H, J_1 = 10 Hz, J_2 = 2 Hz), 3.68 ppm (s, 2 H). Anal. Calcd for $C_{17}H_{12}$: C, 94.44; H, 5.55. Found: C, 94.3; H, 5.6.

Irradiation of Cycloocta[*def*]fluorene (1). A solution of 50 mg (0.23 mmol) of **1** in 200 mL of dry purified cyclohexane was irradiated for 40 min (external, Hanovia 150-W lamp). After evaporation of the solvent, 46 mg of **7** was obtained which exhibited the same spectral properties as those mentioned above.

Preparation of Anions 13 and 14. The hydrocarbon **1** or **5** (ca. 0.1 mmol) was placed in an NMR tube and dissolved in 0.5 mL of THF-d_8. The tube was washed with a stream of argon for 10 min and cooled to –70 °C. *n*-BuLi (0.15 mL) in cyclohexane (3 M) was added, and the tube was sealed. A red color developed slowly. The temperature was then allowed to reach room temperature, and the NMR spectrum was recorded. The field/frequency of the spectrometer (Varian HA-100D) was locked to the cyclohexane band (δ 1.63). The ^{1}H NMR spectrum of cycloocta[*def*]fluorenyl anion **13** is as follows: 7.08 (d, 4 H, J = 8 Hz), 6.38 (t, 2 H, J = 8 Hz), 5.83 (s, 1 H), 5.42 (dd, 2 H, J_1 = 10 Hz, J_2 = 4 Hz), 4.96 ppm (dd, 2 H, J_1 = 10 Hz, J_2 = 4 Hz). The ^{1}H NMR spectrum of the cyclopenta[*def*]phenanthrenyl anion (**14**) is as follows: 7.73 (s, 2 H), 7.41 (m, 4 H), 7.05 (dd, 2 H, J_1 = 8 Hz, J_2 = 2 Hz), 6.06 ppm (s, 1 H).

Quenching of Anions 13 and 14. (a) With H_2O. The contents of the NMR tubes were added to 30 mL of water, extracted with CH_2Cl_2, and evaporated. A quantitative yield of the starting hydrocarbon was obtained.

(b) With D_2O. Under the same conditions, quenching with D_2O of anion **13** quantitatively afforded 11-deuteriocycloocta[*def*]fluorene (**1a**): ^{1}H NMR ($CDCl_3$) 6.83–7.75 (m, 6 H), 5.90 (dd, 2 H, J_1 = 10 Hz, J_2 = Hz), 5.68 (dd, 2 H, J_1 = 10 Hz, J_2 = 2 Hz), 3.65 ppm (s, 1 H); mass spectrum, *m/e* 218, 217, 216, 215, 192, 191, 190. Cyclopenta[*def*]phenanthrenyl anion (**14**) afforded quantitatively 9-deuteriocyclopenta[*def*]phenanthrene (**5a**): ^{1}H NMR ($CDCl_3$) 7.1–7.55 (m, 8 H), 3.86 ppm (br s, 1 H).

Quenching of Anion 14 with MeI. The anion prepared from 250 mg of **5** was quenched with MeI and afforded 240 mg of 9-methylcyclopenta[*def*]phenanthrene (**5b**): ^{1}H NMR ($CDCl_3$) 7.75–7.85 (m, 8 H), 4.40 (q, 1 H, J = 8 Hz), 16.5 ppm (d, 3 H, J = 8 Hz).

Registry No. 1, 60047-82-7; 1a, 72867-25-5; 5, 203-64-5; 5a, 26037-53-6; 5b, 30436-39-6; 6, 60047-83-8; 7, 60047-84-9; 13, 60016-22-0; 14, 23560-20-5.

Aromatization of 1,4-Dihydrobenzocycloalkenes, 1,4-Dihydronaphthocycloalkenes, and Related Systems

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A series of methyl-substituted 1,4-dihydrobenzenes has been prepared, and the rates of oxidation of these molecules by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been measured. Existing evidence points to the involvement of a positively charged intermediate which is formed as an ion pair in an initial rate-limiting hydride transfer to DDQ. Series of cycloalkyl-fused 1,4-dihydrobenzenes and 1,4-dihydronaphthalenes (fused 1,2 and 2,3) have been prepared and the rates of their DDQ induced aromatization have been studied. The results are explained on the basis of inductive effects associated with the size of the fused ring and exocyclic vs. endocyclic bond order preferences.

In an earlier paper we discussed the preparation and properties of bisannelated benzenes in which two small rings are fused either meta or para to one another about the benzene nucleus.[1] Differences in physical properties were observed to depend not only upon the degree of strain imposed on the aromatic nucleus but also upon the position at which this strain is introduced. A simple consideration of Kekulé resonance forms suggests a potential explanation for these differences. In the case of meta-bisannelated benzenes, the two Kekulé forms are nonequivalent, one having the double bonds endocyclic (**1b**) and the other having them exocyclic (**1a**) to the small rings. For the para-fused system (**2**) where $m = n$, both forms are equivalent.

In the case of annelated naphthalenes **3** and **4**, the situation is similar with one important difference. The

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[1] (a) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977); (b) R. P. Thummel, *J. Am. Chem. Soc.*, **98**, 628 (1976); (c) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **43**, 3170 (1978).

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