Manifestation of Dual Aromaticity in Doubly Charged Annelated Pentalenes[1]

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Abstract: 1,9-Dimethyldibenzo[*b,f*]pentalene (**18**) was oxidized and reduced chemically and electrochemically to the respective dication and dianion. The parent hydrocarbon dibenzo[*b,f*]pentalene (**17**) also formed the respective dication and dianion. The dication and dianion showed aromatic diatropicity. The NMR characteristics are discussed in terms of the aromaticity vs. charge effects and the validity of the peripheral model is presented. The electrochemical parameters are discussed in relation to the electronic character of these systems.

Conjugated 4n π-electron monocyclic systems acquire aromatic character by a two-electron oxidation or reduction that leads to the corresponding dications or dianions.[4] In this series derivatives of cyclobutadiene dication (**1**)[5] and dianion (**2**),[6] cyclooctatetraene dication (**3**)[7] and dianion (**4**),[8] and [16]annulenyl dication (**5**)[4] and dianion (**6**)[10] represent the duality of the 4n π-electron system in gaining aromaticity. Although Hückel's rule[11] was originally restricted to monocyclic systems, much interest has been stimulated on the theoretical and experimental aspects of polycyclic systems.[12] Dewar's and Breslow's[12b,13] elegant approach to the prediction of aromaticity in the polycyclic series was based on the application of Hückel's "magic number" of $(4n + 2)$ π electrons to the periphery of the molecule. In this approach the inner bonds of the polycyclic systems were regarded as perturbing bridges (cross-links) of the conjugated periphery. Nonalternant fused conjugated systems may be composed, in principle, of either a $(4n + 2)$ periphery, e.g., azulene (**7**), or a 4n π-electron periphery.[13d] In the latter series the elusive pentalene (**8**) occupies a cardinal position and its antiaromatic π conjugation evoked much theoretical and experimental interest.[14] Although **8** has not yet been prepared, its stabilization by alkyl substitution has been reported.[15] Pentalene (**8**) can be regarded, schematically, as the product of bridging at positions 1 and 5 of the monocyclic 8π system cyclooctatetraene (**9**). Thus, the parallelity between the 8π mono- and bicyclic systems in attaining aromatic character should be raised.[4] From the peripheral presentation it is therefore to be expected that pentalene dication and pentalene dianion will exhibit aromatic character due to peripheral delocalization of 6π and 10π electrons, respectively.

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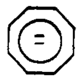

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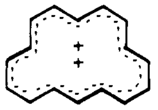

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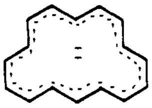

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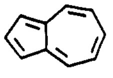

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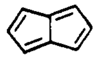

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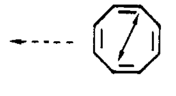

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Very limited information exists on doubly charged ions which originate from 4n π-electron bicyclic conjugated systems. Pentalene dianion (**10**) was prepared by Katz in 1964.[16] Dibenzo[*cd,gh*]pentalene dianion (**11**) was reported by Trost[17] to exhibit diatropic character. Heptalene dianion (**12**)[18] and the recently reported dibenzo[*gh,op*]nonalene dianion (**13**)[19] were also shown to be aromatic. However, in neither of these systems have the expected aromatic dications been reported. Even more so, several attempts to prepare pentalene dication (**14**) and its derivatives have failed. The preparation of hexachloropentalene dication (**14a**) was reported by Kusuda,[20] but the lack of direct proof of its dicationic character and the lack of protons attached to the skeleton prevented the unequivocal tracing of its aromatic character. Protonation of dibenzo[*cd,gh*]pentalene quinone to form **15** was intended to determine the possible contribution of an aromatic dihydroxypentalene dication, viz., **15a**. The finding that the charge was localized at the sites of protonation was attributed to steric hindrance of charge delocalization.[17a] The electrochemical oxidation of tri-*tert*-butylpentalene (**16**) recently published by Johnson[21] resulted exclusively in the formation of the respective radical cation. The fact that the dication was not obtained was rationalized by the antiaromaticity of the two fused cyclopentadienyl cations and was summarized by Johnson[21] as follows: "... The dication generated (16^{2+}) would be a fused pair of cyclopentadienyl dications; the absence of a second oxidation is not surprising". The postulated contribution of antiaromatic components does not exist in the monocyclic series. This discrepancy, if real, emphasizes a fundamental difference between conjugated 4n π monocyclic and bicyclic systems. Moreover, if the antiaromatic contributions of the components are significant then the peripheral aromatic delocalization of the six π electrons may be questioned and it may

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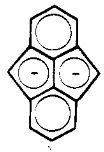

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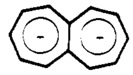

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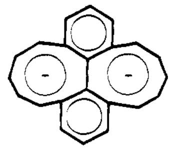

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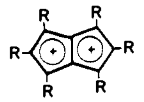
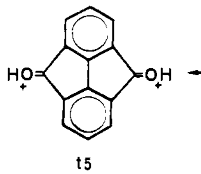


14, R=H
14a, R=Cl



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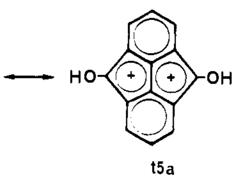

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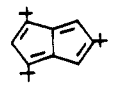

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Table I. ^{1}H NMR Chemical Shifts (ppm) of Hydrocarbons and Dications[a]

system	H_3, H_6, H_{11}, H_{14}	H_4, H_5, H_{12}, H_{13}	H_1, H_9	CH_3
18	6.9[b]			2.17
19	9.84 (d, J = 9 Hz) 9.49 (d, J = 8 Hz)	9.72 (t, J = 7.6 Hz) 9.40 (t, J = 7 Hz)		4.08
$\Delta\delta H_i$[c]	2.94; 2.59	2.82; 2.50		1.91
17	6.9[b]		6.4	
20	9.90 (d, J = 7.4 Hz) 9.52 (d, J = 7.2 Hz)	9.70 (t, J = 7.4 Hz) 9.45 (t, J = 7.2 Hz)	10.1 (s)	
$\Delta\delta H_i$[c]	3.0; 2.62	2.8; 2.55	3.7	

[a] In parts per million downfield from Me_4Si, SO_2ClF at 32 °C, 270 MHz. [b] Center of multiplet. [c] Chemical shift difference between the respective bands of dication and hydrocarbon.

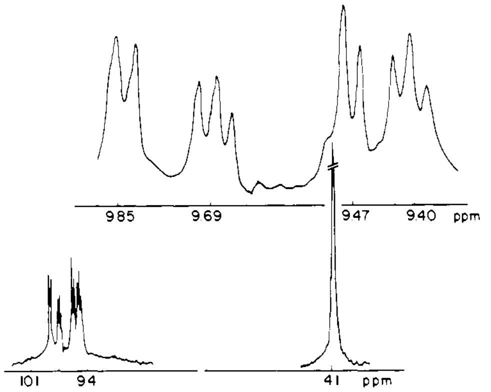


Figure 1. ^{1}H NMR spectrum (ppm, relative to $SiMe_4$) of 1,9-dimethyldibenzo[*b,f*]pentalene dication (**19**). Top: expansion of the benzo protons absorption.

disable the peripheral polycyclic aromatic presentation.[12,13] It should also be noted that all the reported pentalene dianions have been prepared by a double deprotonation process from partially reduced pentalene derivatives.[16,17] However, attempts to reduce **16** chemically or electrochemically failed and only the respective radical anion could be achieved.[21] We present our results on the aromatic character of polycyclic systems which bear doubly charged pentalene moieties and discuss the validity of the peripheral model as a representative of the aromatic polycyclic ions.[1]

Results and Discussion

The failure to characterize the pentalene dication (**14**) is attributed by us to charge repulsions in the small molecular perimeter. This explanation is similar to that proposed to rationalize the difficulties in the formation of the Hückeloid cyclobutadiene[5,22] and cyclooctatetraene dications.[7] These charge repulsions can be overcome by benzene annelation which enables charge delocalization and effectively increases the molecular perimeter, as well as by alkyl substitution which stabilizes inductively the respective cations. The formation of the dianion **10**,[16] which is prima facie influenced by a similar electrostatic repulsion, is rationalized in terms of the specific interactions with the alkali counterions as well as the media used for its preparation (cf. the ease of formation of **4** vs. **3**, vide infra).[7,8] Dibenzo[*b,f*]pentalene (**17**) seems to be a promising model for the study of a system comprising a pentalene moiety. The availability of this system should be noted (vide infra), in contrast to the absence of **8**. Theoretical calculations[23] show a REPE value (resonance energy per π electron) of 0.069 eV for **17** in contrast to a negative value for the parent hydrocarbon **8**. Thus a polyolefinic character of **17** is manifested due to quenching of the antiaromatic character of its pentalene moiety by fusion to benzene rings. Hence, comparison of the chemical shifts of the hydrocarbon with the derived doubly charged species should enable the assignment of the diatropic character of the latter.

1,9-Dimethyldibenzo[*b,f*]pentalene Dication (19) and Dibenzo[*b,f*]pentalene Dication (20). 1,9-Dimethyldibenzo[*b,f*]pentalene (**18**) seemed an adequate substrate for the study of the two-electron oxidation process and the formation of the dication **19**. This substrate combines the previously mentioned stabilizing factors of the positive charges. The starting material, viz., **18**, was prepared by Brand's method,[24] and its treatment with SbF_5 in SO_2ClF resulted in a dark-green solution attributed to the formation of **19**. The ^{1}H NMR spectrum of **19** (Figure 1) shows a considerable downfield shift of all protons (Table I). The methyl groups are shifted downfield by 1.9 ppm, in agreement with the downfield shift of other methyl-bearing aromatic dications.[7,22] The dicationic nature of **19** was deduced from its ^{13}C NMR parameters.[25] A total downfield shift of 368 ppm was observed in the oxidation process **18** → **19**. The Spiesecke and Schneider correlation[25,26] predicts a total downfield shift of ^{13}C bands of 160–200 ppm per unit of positive charge. The observed downfield shift corresponds to 184 ppm/e (368/2 = 184), and is in good agreement with the formation of a doubly charged species, viz., **19**. The ^{1}H NMR spectrum of **19** is influenced by the following factors: (a) deshielding due to the formation of the positive charges, (b) deshielding due to the possible influence of an induced diamagnetic ring current as a result of the formation of an aromatic system.[27] In order to characterize the diatropicity of **19** a differentiation has to be made between these two factors. Table I summarizes the chemical shifts in the oxidation process of **18**. The average change in chemical shifts ($\Delta\delta_H$(av) = $\sum \Delta\delta H_i/_{n_i}$) equals 2.81 ppm for each one of the protons. It has been shown in a variety of nonbenzenoid aromatic ions that a total change in the proton chemical shift of 10.7 ppm per unit of charge is obtained (shielding or deshielding according to the nature of the charge).[27a] Thus, a total proton downfield shift of 21.4 ppm (2 × 10.7) is expected in the oxidation of **18** to **19**, which corresponds to an average downfield shift for each proton of 1.34 ppm (21.4/16). The observed value of the average downfield shift ($\Delta\delta_H$(av) 2.81 ppm) is more than twice as high as the expected value due to charge deshielding. The excess of the downfield shift (1.47 ppm) is therefore attributed[27] to the formation of an induced diamagnetic ring current, as a result of the delocalization of 14π electrons in the periphery of **19** (vide infra). The disadvantage of **19** is the absence of protons linked directly to the pentalene moiety. The development of the diamagnetic ring current in the pentalene component itself could therefore not be followed. This discrepancy was overcome by giving up the inductive stabilizing effect of the methyl groups attached to the pentalene moiety and oxidizing **17**, which still has the stabilizing effect of the dication due to benzene fusion. The parent hydrocarbon, viz., **17**, was synthesized according to Linstead's method from diphenylsuccinindone.[28] Treatment of **17** with SbF_5 in SO_2ClF resulted in the formation of a violet-purple solution attributed

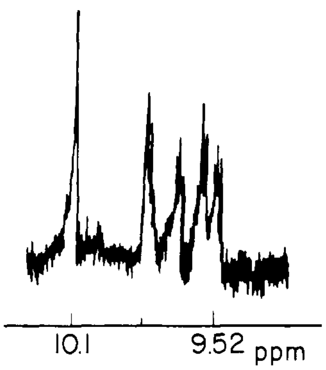
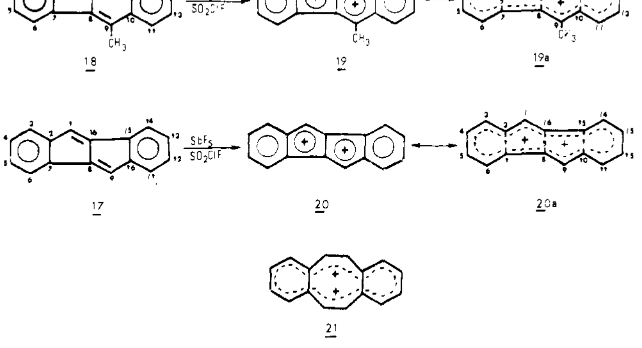


Figure 2. ${}^1H$ NMR spectrum (ppm, relative to $SiMe_4$) of dibenzo[*b,f*]-pentalene dication (**20**).

to the formation of the dibenzo[*b,f*]pentalene dication (**20**). The ${}^1H$ NMR spectrum (Figure 2) reveals a significant downfield shift of 342 ppm. This is the value expected by the Spiesecke-Schneider correlation[26] for a positive doubly charged species (171 ppm/e). Table I summarizes the chemical shifts observed in the oxidation process **17** → **20**. It may be seen that all the protons were significantly shifted to low field and the average downfield shift $\Delta\delta_H(av)$ is 2.9 ppm per each proton. The highest downfield shift is observed in protons H_1 and H_9, which are the protons attached to the pentalene nucleus. The average downfield shift is of the same magnitude as observed in **19**. The small difference (0.1 ppm) may be ascribed to an excess of deshielding owing to the absence of the inductive effect of the methyl groups in **20**. Here again, the expected total downfield shift of the protons due to charge deshielding of **20** is 21.4 ppm (10.7 × 2) or 1.34 ppm per proton (21.4/16).[27] The excess (1.6 ppm) of the downfield shift is related to the formation of an induced diamagnetic ring current. The significant downfield shift observed for H_1 and H_9 (Table I) cannot be attributed to charge deshielding only (vide infra), thus exhibiting the presence of a diamagnetic ring current in the pentalene dication component.[27]

The benzene ring protons of **19** and **20** have shifted to a higher extent than predicted for the effect of charge deshielding only. This suggests that charge delocalization as well as an induced diamagnetic ring current is operating over the whole framework. Furthermore, the average ${}^{13}C$ NMR chemical shift (δ ${}^{13}C(av)$) is 154.7 ppm for **19** and 156.2 ppm for **20**, a similar value to that observed in the monocyclic [16]annulene dication **5**[9] (δ ${}^{13}C(av)$ 154.3 ppm), and in the isoelectronic dibenzo[*a,e*]cyclooctatetraene dication (**21**) (δ ${}^{13}C(av)$ 153.6 ppm).[7b,9,29] In addition, the average proton downfield shifts in the processes **18** → **19** and **17** → **20** (2.8 and 2.9 ppm, respectively) correspond to the value observed in the oxidation process to dication **21**.[7b] These phenomena suggest that dibenzo[*b,f*]pentalene dication **20** and 1,9-dimethyldibenzo[*b,f*]pentalene dication (**19**) should be regarded as perturbed peripheral [16]annulene dications. The aromatic diatropic character of the two cations, viz., **19** and **20**, as a result of the 14π electron delocalization over 16 carbon atoms (14π 16C systems) strengthens both the peripheral model and the representation of our systems as [16]annulene dicationic frames bridged by three σ bonds, viz., **19a** and **20a**, respectively.[4,13]



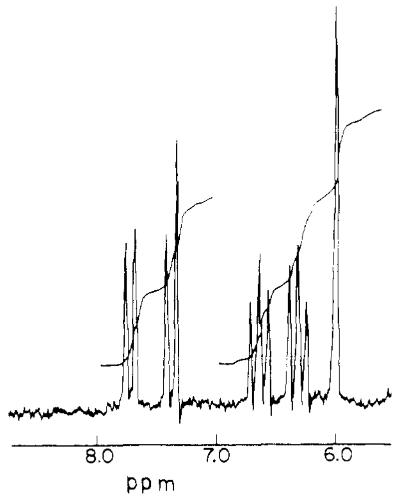


Figure 3. ${}^1H$ NMR spectrum (ppm, relative to $SiMe_4$) of dibenzo[*b,f*]-pentalene dianion (**22**).

Dibenzo[*b,f*]pentalene Dianion (22) and 1,9-Dimethyldibenzo[*b,f*]pentalene Dianion (23). The duality in gaining aromaticity of nonalternant polycyclic conjugated 4n π electron systems can be manifested by two-electron oxidation and reduction to the corresponding dicationic and dianionic systems. Following the formation of the dications **19** and **20**, we investigated the characteristics of the dianions **22** and **23**. The characterization of aromaticity in these dianions should show an unqualified parallelity to the conjugated monocyclic 4n π electron series.[4]

Treatment of 1,9-dihydrodibenzo[*b,f*]pentalene (**24**)[30] in THF-d_8 with *n*-butyllithium resulted in the formation of a dark violet solution assigned to dibenzo[*b,f*]pentalene dianion (**22**).[31] Quenching of **22** with D_2O or methyl iodide produced **25** and a mixture of **26a** and **26b**, respectively, pointing to a *double* electrophilic attack on the negatively charged species. The ${}^1H$ NMR spectrum of **22** (Figure 3) consists of a singlet at 5.9 ppm (H_1 and H_9) and an ABCD spectrum of the benzene ring protons (Table II). The chemical shifts of **22** are influenced by two opposing parameters:[27] (a) shielding due to the negative charges and (b) deshielding due to the formation of the expected induced diamagnetic ring current as a result of the 18 π electron delocalization. The correlation of Schaeffer and Schneider predicts[27a] a total shielding of 21.4 ppm (10.7 × 2) of the protons, as a result of the formation of two negative charges, or an average shielding of 1.34 ppm for each proton (21.4/16) so that the center of gravity of the proton shifts is expected to be shielded to an extent of ca. 1.34 ppm. As can be seen from Table II the average chemical shift as a result of the formation of **22** did not change ($\Delta\delta_H(av) = \sum\Delta\delta H_i/n_i \approx 0$).

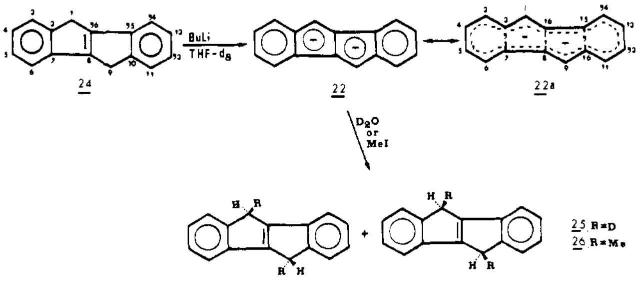


Table II. ^1H NMR Chemical Shifts (ppm) of Hydrocarbons and Dianions[a]

system	H_3, H_6, H_{11}, H_{14}	H_4, H_5, H_{12}, H_{13}	H_1, H_9	CH_3
17	6.9[b]		6.4	
22	7.65 (d, J = 8 Hz)	6.80 (dd, J_1 = 8, J_2 = 6 Hz)	5.9 (s)	
	7.24 (d, J = 8 Hz)	6.54 (dd, J_1 = 8, J_2 = 7 Hz)		
$\Delta\delta H_i$[c]	0.75; 0.34	−0.1; −0.26	−0.5	
18	6.9[b]			2.17
23	7.57 (d, J = 7 Hz)	7.17 (t, J = 7 Hz)		3.10 (s)
	7.27 (d, J = 8 Hz)	6.91 (t, J = 8 Hz)		
$\Delta\delta H_i$[c]	0.67; 0.37	0.27		0.93

[a] In parts per million downfield from Me_4Si, THF-d_8, 100 MHz. [b] Center of multiplet. [c] Chemical shift difference between the respective bands of dianion and hydrocarbon.

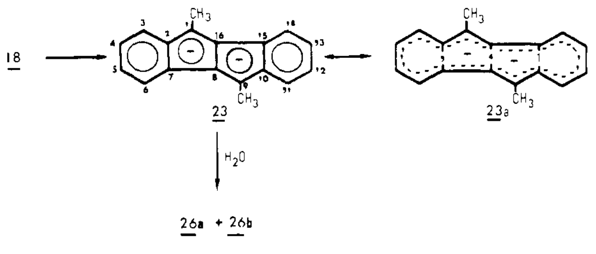
Table III. Experimental and Calculated Charge Densities of Dibenzo[*b,f*]pentalene Dication **20** and Dianion **22**

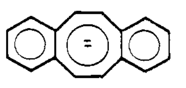
	20					**22**				
position[a]	$\Delta\delta_i$[b]	σ_i[c]	$\Delta\delta_i + \sigma_i$	ρ_i (exptl)[d]	ρ_i(calcd)[e]	$\Delta\delta_i$[b]	σ_i[c]	$\Delta\delta_i + \sigma_i$	ρ_i (exptl)[d]	ρ_i (calcd)[d]
1	−2.81	1.06	−1.75	0.836	0.844	1.39	1.06	2.45	1.229	1.246
3	−2.16	0.65	−1.51	0.859	0.926	0.05	0.65	0.70	1.065	1.076
4	−2.41	0.27	−2.14	0.800	0.865	0.49	0.27	0.76	1.071	1.068
5	−2.23	0.29	−1.94	0.819	0.908	0.75	0.29	1.04	1.097	1.109
6	−2.61	0.72	−1.84	0.823	0.914	−0.36	0.72	0.36	1.033	1.054

[a] Positions are as indicated in the structure. [b] Chemical shift relative to the benzene proton shift (δ 7.29 ppm). [c] Values taken from ref 31b. [d] ρ_i (exptl) = 1 + $\Delta\rho_i$, $\Delta\rho_i$ calculated according to eq 2. [e] Calculated by the ωβ-HMO method.[33]

It can be assumed therefore that an effect contradictory to the negative charge shielding is operative. This countereffect which nulls the charge influence is rationalized by the formation of an induced ring current due to the aromaticity gained in **22**. Protons H_1 and H_9 (of the five-membered rings) are shielded to the greatest extent (Table II), in accordance with HMO calculations that point to the highest charge localization at C_1 and C_9 (vide infra) and as found in the quenching experiments. Despite the negative charge, protons H_3, H_6, H_{11}, and H_{14} are deshielded establishing that the formed diamagnetic ring currents are operative over the perimeter of the system. Dibenzo[*b,f*]pentalene dianion (**22**) should be regarded as a peripheral aromatic [16]annulene dianion with delocalization of 18 π electrons and cross-linked by three perturbing σ bonds, viz., **22a**. The proton chemical shift of **22** are reminiscent of the chemical shifts of dibenzo[*a,e*]cyclooctatetraene dianion (**27**),[32] thus supporting the peripheral presentation.

Pentalene dianionic systems were so far prepared by deprotonation of a dihydropentalene derivative only.[16,17,31] To investigate the process parallel to the two-electron oxidation described above we carried out a metal reduction of 1,9-dimethyldibenzo[*b,f*]pentalene (**18**). The reaction of **18** with lithium metal in THF-d_8 gave a dark-red solution assigned to 1,9-dimethyldibenzo[*b,f*]pentalene dianion (**23**), after prolonged contact (14 h). The proton chemical shifts of **23** and the coupling constants (Table II) resemble those of **22**. Quenching of **23** with water gave a mixture of isomers of 1,9-dimethyl-1,9-dihydrodibenzo[*b,f*]pentalene, i.e., **26a** and **26b**, identical with the quenching product of **22** with methyl iodide. The average proton shifts of the perimeter of **23** Table II) is $\Delta\delta_H$(av) 0.34 ppm; thus the opposing effect of the diamagnetic deshielding relative to the shielding due to the charge is even more conspicuous in this system.[27] The fact that the benzene protons are deshielded despite the negative charge points to an aromatic peripheral delocalization, viz., **23a**. It should be emphasized that the average contribution to the chemical shift due to the diamagnetic ring current in **19**, **20**, **22** and **23** is similar in magnitude (1.46 and 1.56 ppm, respectively); thus the aromatic character of the two couples of doubly charged molecules is similar.





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It has previously been shown that the difference in proton chemical shifts of Hückeloid charged systems is directly proportional to the difference in charge densities on the carbon atoms to which these protons are attached. Owing to diamagnetic ring currents of the adjacent rings on the proton chemical shifts of the ring under study (σ_i), a correction should be added to the charge effect in the polycyclic series as follows:[27a]

$$\Delta\delta_i = K\Delta\rho_i - \sigma_i \qquad (1)$$

When benzene is chosen as the reference compound (ρ_i = 1), eq 1 can be rewritten as follows:

$$\Delta\delta_i = K(\rho_i - 1) - \sigma_i \text{ or } \rho_i - \frac{\Delta\delta_i + \sigma_i}{K} + 1 \qquad (2)$$

Proton chemical shifts can thus allow charge density calculations (ρ_i) on their attached carbon atoms. Table III summarizes the charge densities of **20** and **22** calculated by this method and compared with the calculated charge densities by iterated MO calculations.[33] Owing to the similarity of the aromatic character of the two ions **20** and **22** as evaluated by their NMR spectra we could choose similar parameters σ_i's which express the diamagnetic contributions of the doubly charged pentalene moieties on the benzene ring protons.[27a,31b] Table III shows that there is good agreement between the experimental and calculated values and further supports the similarity of the aromatic character of the two ions.

Electrochemical Studies. Further insight into the electronic characteristics of dibenzo[*b,f*]pentalenes can be gained by

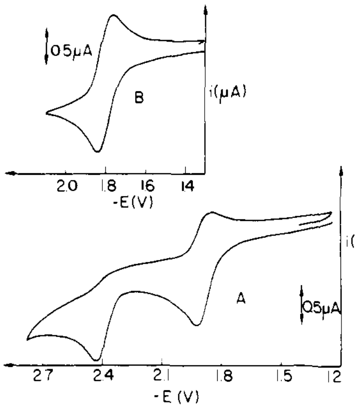


Figure 4. Cyclic voltammograms of the reduction of 1,9-dimethyldibenzo[*b,f*]pentalene (**18**) (2.35 mM) in DMF, under nitrogen (0.1 N Et_4NClO_4) at room temperature, 100 mV/s sweep rate. A (bottom): potential scan −1.2 to −2.8 V, vs. Ag/Ag$^+$ reference electrode. B (top): potential scan −1.3 to −2.0 V, vs. Ag/Ag$^+$ reference electrode.

Table IV. Cyclic Voltammetric Data of the Reduction of 1,9-Dimethyldibenzo[*b,f*]pentalene (**18**) to the Radical Anion **28a** as a Function of Voltage Sweep Rate[a]

V, mV/s[b]	$i_{p_c}/v^{1/2}$ CA	i_{p_a}/i_{p_c}[c]	$E_{p_c} - E_{p_a}$,[d] mV
50	0.67[e]	0.94	73
100	0.63	0.94	70
200	0.60	0.92	68
500	0.61	0.88	70

[a] [**18**] = 2.35 mM in DMF-(n-Bu)$_4$NClO$_4$ (0.1 M) at room temperature. [b] Voltage sweep rate. [c] The deviations from unity could result from errors in estimating the base line of i_{p_a}. [d] Though the peak separation is slightly higher than the theoretical value (60 mV) for a reversible one-electron transfer, its constancy over the entire range of the applied sweep rates points to electrochemical reversibility, possibly accompanied with a minor chemical reaction). [e] All figures in this column have the unit of: A cm^2 V$^{-1/2}$s$^{1/2}$ M^{-1}.

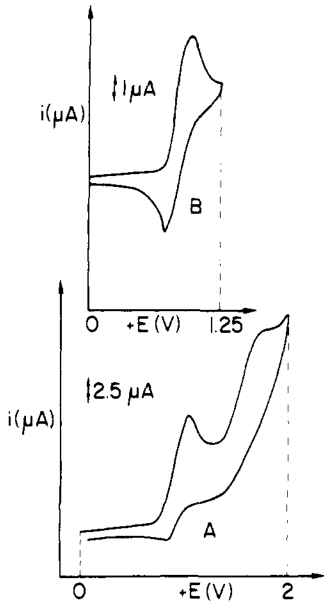


Figure 5. Cyclic voltammograms of the oxidation of 1,9-dimethyldibenzo[*b,f*]pentalene (**18**) (9.4 mM) in AN, under nitrogen (0.1 N Et_4NClO_4). A (bottom): at room temperature, sweep rate 2.0 V/s. Potential scan 0.0-2.0 V, vs. Ag/Ag$^+$ reference electrode. B (top): at −35 °C sweep rate 1.0 V/s. Potential scan 0.0-1.25 V, vs. Ag/Ag$^+$ reference electrode.

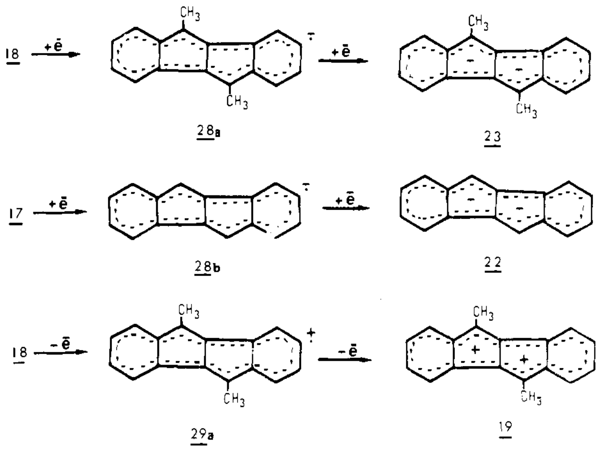
Table V. Voltammetric Data for the Reduction of 16π Electron Conjugated Hydrocarbons in Dimethylformamide[a]

hydrocarbon	$E_{p_c}{}^1$	$E_{p_c}{}^2$
dibenzo[*b,f*]pentalene (**17**)	−1.40[b]	−1.98[b]
benz[*a*]anthracene	−1.96[c]	−2.65
chrysene	−2.225[c]	−2.730

[a] Relative to SCE reference electrode. [b] Corrected relative to SCE. [c] From ref 38b.

electrochemical studies.[34] The first reduction potential represents qualitatively the energy required to introduce an electron to the LUMO level whereas the first oxidation potential corresponds to the energy required to remove an electron from the HOMO level. As a result, the HOMO-LUMO separations of the orbitals operative in gaining the aromatic character of the respective dianions and dications can thus be studied.[35] Cyclic voltammetry[36] of **18** in the region 0 to −2.8 V (vs. Ag/Ag$^+$ reference electrode) showed two one-electron reduction waves at $E_{p_c}{}^1 = -1.92$ V and $E_{p_c}{}^2 = -2.43$ V, respectively (Figure 4). The first reduction wave, attributed to the one-electron reduction which forms the respective radical anion (**28a**),[37] is reversible (Table IV). The second reduction wave corresponds to the reduction of **28a** to 1,9-dimethyldibenzo[*b,f*]pentalene dianion (**23**) and is irreversible. The cyclic voltammetry of **17** at −60 °C in the region 0 to −2.8 V (relative to Ag/Ag$^+$ reference electrode) showed two reduction waves at $E_{p_c}{}^1 = -1.65$ V and $E_{p_c}{}^2 = -2.23$ V. The first reduction wave, which corresponds to the respective radical anion (**28b**), showed electrochemical reversibility at a scan rate of 100 mV/s ($E_{p_c}{}^1 - E_{p_a}{}^1$ = (60 mV) while the second wave of reduction to form the dianion **22** is irreversible. The irreversibility of the electrogenerated aromatic dianions reflects their chemical reactivity.[35] It is known that "spontaneous protonation of electrogenerated dianions of aromatic hydrocarbons is so rapid that no other reactions are known".[38] As the first reduction potential represents the energy required to introduce an electron to the LUMO level, we expect, as a result of aromatic stabilization, a lowered reduction potential. This reduction potential has been compared with that of related conjugated polycyclic systems containing 18π electrons in which the corresponding dianions do not have aromatic character[38b] (Table V). It may be seen that this prediction is realized and that the reduction potential of **17** is significantly lower than that of the 18-electron benzene-fused hydrocarbons (ca. 0.7 V), pointing to the thermodynamic stabilization of **22.** Further support for this conclusion comes from the similarity of the reduction potentials of **17** and that of the isoelectronic dibenzo[*a,e*]cyclooctatetraene, where its derived dianion **27** also exhibits aromatic character.[39] Although **17** is nonalternant, the first reduction potential of **17** ($E_{p_c}{}^1 = -1.40$ V) correlates nicely with the value predicted by Hoijtink[34,40] applying the β coefficient of the LUMO orbital ($E_{p_c}{}^1 = -1.46$ V when $m_{\mathrm{LUMO}} = -0.23$).

Cyclic voltammetry of **18** in the region 0-2.0 V (at room temperature, relative to Ag/Ag$^+$ electrode) resulted in two one-electron irreversible oxidation curves at $E_{p_a}{}^1 = 0.98$ V and $E_{p_a}{}^2 = 1.5$ V (Figure 5A). When the cyclic voltammetry was conducted at −35 °C in the region 0-1.25 V and at a scanning rate of 5 V/s, the first oxidation curve at $E_{p_a}{}^1 = -0.98$ V turned out to be quasi-reversible and the respective reduction potential of the electrogenerated species was observed at $E_{p_c}{}^1 = 0.85$ V (Figure 5B). The first oxidation potential is attributed to the formation of the radical cation **29a**[37] while the second oxidation at $E_{p_a}{}^2 = 1.5$ V represents the oxidation to **19.** No conclusive deductions could be reached from the anodic oxidation of **17.** In methylene chloride-trifluoroacetic acid media it polymerized and in acetonitrile it caused electrode filming and gave ill-defined waves in the region of 1-1.6 V.



The difference between the first oxidation and the first reduction potentials of **18** represents the LUMO-HOMO energy separation:

$$E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} = \Delta \mathrm{MO} = E_{\mathrm{ox}} - E_{\mathrm{red}}$$
$$= 0.98 - (-1.92) = 2.90\ \mathrm{V} \quad (3)$$

This relatively low-energy difference of the LUMO-HOMO separation correlates nicely[13d,14] with the low value of the above-mentioned energy separation of monocyclic 4n π conjugated systems, e.g., cyclooctatetraene, thus lending strength to the aromatic character of the dication **19** and the dianion **23**.

Conclusions

The easy two-electron oxidation of dibenzo[*b,f*]pentalenes by chemical and electrochemical methods into the respective dicationic species supports the hypothesis that the failure to prepare pentalene dication (**14**) lies in charge repulsions existing in the small molecular perimeters rather than in antiaromatic contribution of its five membered ring components.[21] These species, i.e., **19** and **20**, are the first systems which bear a pentalene dicationic component. The conspicuous aromatic character of these dications derived from proton chemical shifts[27] emphasizes the significance of the peripheral electron delocalization vs. the skeletal contributions. The dianions **22** and **23** were prepared by chemical (deprotonation and reduction) and by electrochemical methods, and represent the first preparation of a pentalene dianion derivative by metal reduction. The ^{1}H NMR parameters demonstrate that the dianions show an induced ring current and behave as expected for aromatic species.[27] It appears that the duality of aromatic character of nonalternant bicyclic 4n π electron systems resembles the behavior of the parallel monocyclic 4n π series.[4]

The chemical shift parameters of the doubly charged species as well as theoretical calculations support similar aromatic characteristics of the dications and the dianions. The NMR data and the charge density calculations suggest a charge delocalization over the entire periphery and the formation of the respective aromatic diatropic systems due to 14π and 18π electron delocalizations. The generality of the peripheral model in predicting the aromaticity of polycyclic ions has been demonstrated. The electrochemical parameters point to the electronic characteristics of the HOMO and LUMO orbitals responsible for the dual aromatic character of the benzannelated pentalenes. These results suggest that a variety of polycyclic doubly charged aromatic systems should be available thus extending new homologous polycyclic aromatic series parallel to the monocyclic Hückeloid series.

Experimental Section

^{1}H NMR spectra were obtained (5-mm samples) on either a Varian Associates Model HA 100 D (CW method) or a Bruker WH-270 supercon spectrometer (FT method). The field/frequency regulations were maintained by locking to either external (capillary) Me_4Si in the CW instrument or to external (capillary) acetone-d_6 in the deuterium locked FT instrument. The chemical shifts are reported downfield relative to Me_4Si. On the WH-270 instrument, the free induction decay signal derived after each pulse was digitized and accumulated on a NIC-1180 computer (16K). Fourier transform of the accumulated FID signals gave the frequency spectrum. All these instruments are equipped with variable temperature accessories.

^{13}C NMR spectra were obtained (8-mm samples) on a Varian Associates CFT-20 spectrometer (FT method). The spectrometer is equipped with a broad band proton decoupler and a variable temperature probe.

Mass spectra were obtained with an Varian-MAT 311 instrument at 70 eV. Melting points were taken on a Fisher-Johns apparatus (uncorrected).

Cyclic voltammetry was performed using a Princeton Applied Research (PAR) Model 173 instrument. A universal programmer Model 175 (PAR) was used as a triangle function wave generator and for the determination of scan rates during cyclic voltammetric measurements. The recorder enployed was a Bryans Model 26000-A4 *X-Y* recorder, and a Tektronix 5103N oscilloscope with a storage memory unit.

Materials. 1,9-Dimethyldibenzo[*b,f*]pentalene (**18**) (mp 212 °C, lit.[24] 212 °C), dibenzo[*b,f*]pentalene (**17**) (mp 273-280 °C, lit.[28] 275-280 °C), and 1,9-dihydrodibenzo[*b,f*]pentalene (**24**) (mp 204 °C, lit.[30] 204-208 °C) were prepared according to literature procedures. Antimony pentafluoride (spectrograde, Cationics Inc.) was distilled prior to application. Acetonitrile (AN) (Fluka, 99.5% purity) was distilled from $KMnO_4$-Na_2CO_3 followed by distillation over P_2O_5 under nitrogen and stored over 4Å molecular sieves. Dimethylformamide (DMF) (Aldrich, Gold Label) was distilled from CaH_2 and stored under nitrogen over 4 Å molecular sieves. Tetrabutylammonium perchlorate (TBAP) (Fluka, Purum grade) was used without further purification. SO_2ClF (Cationics Inc.) was used without further purification. Commercial *n*-butyllithium (in hexane) (Foote Inc.) or *n*-butyllithium in cyclohexane (5 M) prepared from butyl chloride and lithium wire and filtered were used in the deprotonation experiments.

Chemical Oxidation of Dibenzo[*b,f*]pentalenes. The hydrocarbons (5 mg) were suspended in SO_2ClF (0.6 mL) in the 5-mm NMR tube and cooled to −78 °C under argon. A tenfold excess of SbF_5 was added portionwise while vigorously vibrating the cooled NMR tube. After the formation of a clear colored solution, the reference-lock capillary was introduced and the tube was sealed. The temperature of the sample was then allowed to rise to room temperature very slowly (caution) and the proton spectrum was recorded. The preparation of the ^{13}C samples was carried out as follows. To a suspension of the hydrocarbon in SO_2ClF was added SbF_5 as described, at −30 °C to follow the formation of the dications. The solution was then transferred (under argon) to the ^{13}C NMR tube and concentrated with a stream of argon to drive away the excess solvent. After the reference capillary was introduced the tube was sealed and the spectrum was recorded. ^{13}C NMR data for **18**, δ ppm 155, 146.9, 140, 139.4, 131, 130.7, 125.5, 124.4, 15.6; for **19**, δ ppm 171.7, 168.4, 165.1, 162.9, 158.6, 156.2, 145, 140.3, 24.3; for **17**, δ ppm 146.2, 142.7, 140, 136.6, 132.2, 130.9, 127.6, 125.1; for **20**, δ ppm 169.4, 165, 161.3, 157.1, 154.8, 151.9, 147.4, 146.1.

Deprotonation of 1,9-Dihydrodibenzo[*b,f*]pentalene (24). A solution of **24** (15 mg) in THF-d_8 (0.3 mL) was cooled to −78 °C and 0.3 mL of a solution of *n*-butyllithium (cyclohexane, 5 M) was added under argon. The mixture was cooled and the resulting dark violet solution was cautiously allowed to reach room temperature.

Chemical Reduction of 1,9-Dimethyldibenzo[*b,f*]pentalene (18). A solution of **18** in THF-d_8 (0.8 mL) was introduced into a 5-mm NMR tube connected with a side arm to a 3-mL flask containing 60 mg of lithium wire. A sintered glass filter was fitted in the side arm between the tube and the flask. The system was flushed with nitrogen and sealed. The solution of **18** was then brought in contact with the lithium wire and a green color started to develop after 1 h. After 14 h of reaction between the metal and the hydrocarbon the color turned dark red. The solution was then introduced into the NMR tube via the sintered glass filter and the tube was disconnected and sealed.

Electrochemical Experiments. The electrochemical measurements were recorded in a 10-mL cell using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The Ag/0.1 M $AgNO_3$

reference electrode was separated from the working electrode by a glass frit. The auxiliary electrode was cylindrical platinum gauze, and the working electrode was a platinum wire sealed in glass and ground smooth, making a small platinum button. The solutions were degassed by bubbling nitrogen and continuously flushed with nitrogen. The electrochemical reductions were carried out in DMF using neutral alumina to improve the background currents. Compound **18** (2.35 mM) was reduced at room temperature, and **17** (1.12 mM) at −60 °C. The oxidations were performed in acetonitrile (AN) applying 9.4 mM of **18** and 1.78 mM of **17**, respectively, at −40 °C.

Quenching Experiments. A solution of **24** (45 mg) in 7 mL of dry THF was cooled to −78 °C and stirred under nitrogen. A solution of 1 mL of *n*-butyllithium (cyclohexane, 5 M) was added dropwise with the aid of a syringe. The resulting dark violet solution was cautiously allowed to warm up to room temperature and further stirred for 30 min. The solution was cooled again to −30 °C and quenched with D_2O (2 mL) or CH_3I (1.5 mL). After the usual workup **25** and **26a,b** (cis and trans mixture of isomers) were afforded quantitatively. The ^1H NMR spectrum of **25:** δ ($CDCl_3$) 7.1–7.35 (m, 8 H), 3.53 (broad singlet, 2 H). The MS of **25:** *m/e* 207, 206 (M, 100%), 205, 204, 203, 202.

^1H NMR spectrum of **26a,b:** δ ($CDCl_3$) 7.12–7.38 (m, 8 H), 3.64 (m, 2 H), 1.64 and 1.38 (d, 3 H, J = 8 Hz). MS of **26a,b:** *m/e* 233, 232 (M, 100%), 231, 230, 217, 202.

The solution of 1,9-dimethyldibenzo[*b,f*]pentalene dianion **23** was poured on 10 mL of water and extracted with dichloromethane. The separated organic layer was washed with water, dried, and evaporated. The residue of 1,9-dimethyldihydrodibenzo[*b,f*]pentalene **26a,b** (cis and trans mixture) was identical with the CH_3I quenching product of **22**.

Acknowledgment. The ^1H NMR spectra at 270 MHz were recorded on the instrument of the Weizmann Institute of Science, Rehovot.

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