

NOVEL AROMATIC CATIONS AND ANIONS: AROMATICITY-STRUCTURE RELATIONSHIPS

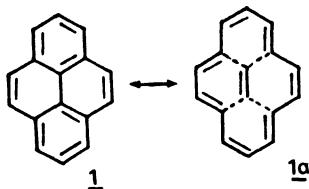
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Abstract - In aromatic polycyclic systems both the local contribution of the components and the peripheral π -delocalization influence the net aromatic nature of the system. Polycyclic conjugated systems are classified according to the number of π -electrons involved in each ring. A $(4n_1 + 2)\pi + (4n_2 + 2)\pi$ fusion results in a $(4n + 2)\pi$ periphery. Indeed, these systems have aromatic character. However, steric effects (e.g. peri H-H interactions and biphenyl backbone) influence the gradual formation of the aromatic ions and direct their stereochemistry. A $(4n_1 + 2)\pi + 4n_2\pi$ fusion results in an antiaromatic $4n\pi$ periphery. The fusion of a cyclopentadienyl anion to a planar COT component in a polycycle shows paratropic character. Oxidation of a polycyclic molecule which includes a planar COT component yields an aromatic system which includes a COT⁺⁺ moiety. The fusion of $4n_1\pi + 4n_2\pi$ systems represents an aromatic $(4n + 2)\pi$ periphery, while the components are antiaromatic. The preparation of benzannelated pentalene dications shows that they exhibit diatropicity and that the peripheral $(4n + 2)\pi$ delocalization dominates. The two electron oxidation and reduction of dibenzopentalenes to the respective aromatic dications and dianions show that $4n\pi$ conjugated polycycles behave similarly to the corresponding monocycles in attaining aromatic character.

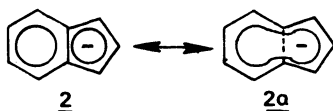
INTRODUCTION

The study of the monocyclic non-benzenoid Huckeloid series established a field of challenging synthetic and theoretical efforts (1). However, the aromaticity of polycyclic π -conjugated frameworks requires further insight. One of the basic problems of the polycyclic systems is best visualized with one of the oldest "aromatic" molecules, i.e. pyrene (1). This system is considered to be aromatic despite the non-Huckeloid conjugation of 16π electrons. Two approaches were suggested to account for the aromaticity of poly-fused conjugated ring systems. One approach considers the partial aromatic contributions of the rings composing the polycycle (2). The second, coined as the "peripheral model," emphasizes the peripheral π -conjugation, while the bridging bonds of the polycycle are considered as a cross-linked perturbation on the conjugated periphery (3). Based on the latter, the aromaticity of pyrene (1) originates from a "Huckeloid" 14π -peripheral delocalization perturbed by an "ethylenic bridge," 1a. Although the aromaticity of pyrene may be satisfactorily explained by either of these two theories, several limitations become apparent when these concepts are applied to more complex systems.

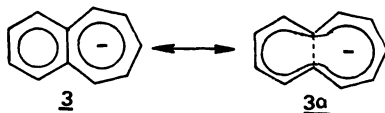


Our objectives in recent years were directed towards gaining insight into the aromaticity of charged polycyclic systems. As we shall see, we are confronted by new phenomena that are important in attaining aromaticity in polycyclic systems and that are non-existing in the monocyclic non-benzenoid series.

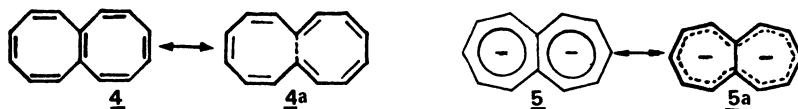
Conjugated polycyclic systems can be classified according to three different modes of fusion: (a) The fusion of a $(4n_1 + 2)\pi$ ring with a second Huckeloid $(4n_2 + 2)\pi$ ring system results in a polycycle that includes a $(4n + 2)\pi$ periphery, while each component contributes aromatic character. Indenyl anion (2) represents this type of fusion, as it includes a 10π conjugated periphery and two 6π aromatic contributions.



(b) The fusion of a $(4n_1 + 2)\pi$ ring with an antiaromatic $4n_2\pi$ system results in a peripheral $4n\pi$ delocalization. However, the components contribute contradicting aromatic and antiaromatic character to the nature of the entire system. Benzocycloheptatrienyl anion (3) represents this type of fusion (4).



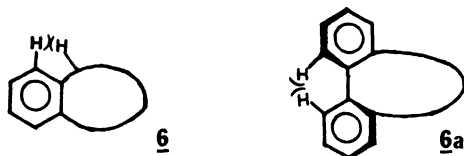
(c) The fusion of two antiaromatic rings ($4n_1\pi + 4n_2\pi$) yields an aromatic $(4n + 2)\pi$ conjugated periphery, while the components yield two antiaromatic contributions. Octalene (4) (5) with a 14π periphery or heptalene dianion (5) (6) with a 10π conjugated periphery, represent this type of fusion.



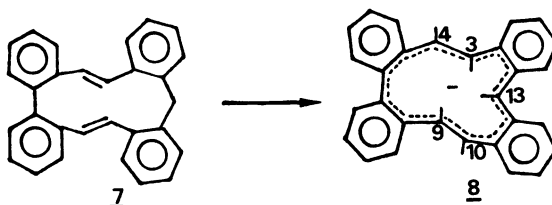
In the last two groups it may be questioned whether the contributions of the components viz. 4 and 5 or the peripheral conjugation 4a and 5a are dominant in characterizing the system.

STERIC EFFECTS IN $(4n + 2)\pi$ PERIPHERIES

The $(4n_1 + 2) + (4n_2 + 2)\pi$ ring fusion is indeed characterized by aromatic character. However, several steric effects were shown to play an important role in the efficiency of π -overlap as well as in the stereochemistry of the resulting aromatic species. In particular, these steric effects are significant when one of the components in the polycycle is a medium-sized ring. Two important effects are *peri* H-H repulsions along the periphery (6) (7) and *ortho* interactions in a biphenyl backbone (6a). These are expected to introduce steric strain in a planar structure, thus perturbing an efficient π - π overlap in the polycycle (8).



An illuminating example that demonstrates the importance of the steric effects operative in polycyclic aromatic systems is observed in the deprotonation of tetrabenzotrans,trans-[13]-annulene (7) (8,9). The NMR spectrum of 7 reveals that the molecule is in a flexible structure, whereby an averaged equivalence of the olefinic bonds is achieved. However, its derived aromatic[13]annulenyl anion (8) appears to be in a fixed distinct structure. The NMR spectrum of 8 reveals three different kinds of protons present in the "inner" paratropic region of the aromatic periphery: two highfield doublets of protons, H_3 and H_9 , and a highfield singlet for proton H_{13} . The resulting configuration of the anion 8 is attributed to a "self-recognition" property of the system to direct its structure into the most favored spatial arrangement. The two *trans* bonds are forced into opposite directions in order to minimize interplanar H-H repulsions (which should be emphasized in a H_4 , H_9 "inner" configuration). In turn, proton H_{13} is flipped into the periphery in order to prohibit two pairs of *peri* H-H repulsions with the adjacent benzene rings.



The role of the biphenyl backbone in influencing the aromaticity of a polycyclic system was demonstrated in the deprotonation of dibenzocyclononatetraenes (CNT) (8). The deprotonation of 1,2:5,6-dibenzo-CNT(9) immediately yields the aromatic diatropic anion 10 (10). However, deprotonation of the isomeric hydrocarbon, 1,2:3,4-dibenzo-CNT(11) (8,11) is accompanied by the initial formation of a non-aromatic partially delocalized anion 12, which undergoes a gradual process to form the planar aromatic, diatropic anion 13. The intermediate formation of 12 is attributed to a steric barrier introduced by biphenyl *ortho* interactions. A similar behavior is observed in the deprotonation of 14 to dibenzo[gh,op]nonalene dianion (15) (12). The initial formation of a non-aromatic, non-planar partially delocalized dianion 16 is observed. Based on its NMR characteristics (Figure 1A), a double pentadienyl anionic delocalization is attributed to 16. The non-planar dianion 16 undergoes a gradual modification and the formation of a new species is observed. The proton NMR spectrum of the new product (Figure 1B) and its quenching products confirm the formation of dibenzo[gh,op]nonalene dianion (15). The low field shifts observed in 15 as compared to those of the non-planar dianion 16 reveal that 15 exhibits diatropic aromatic character.

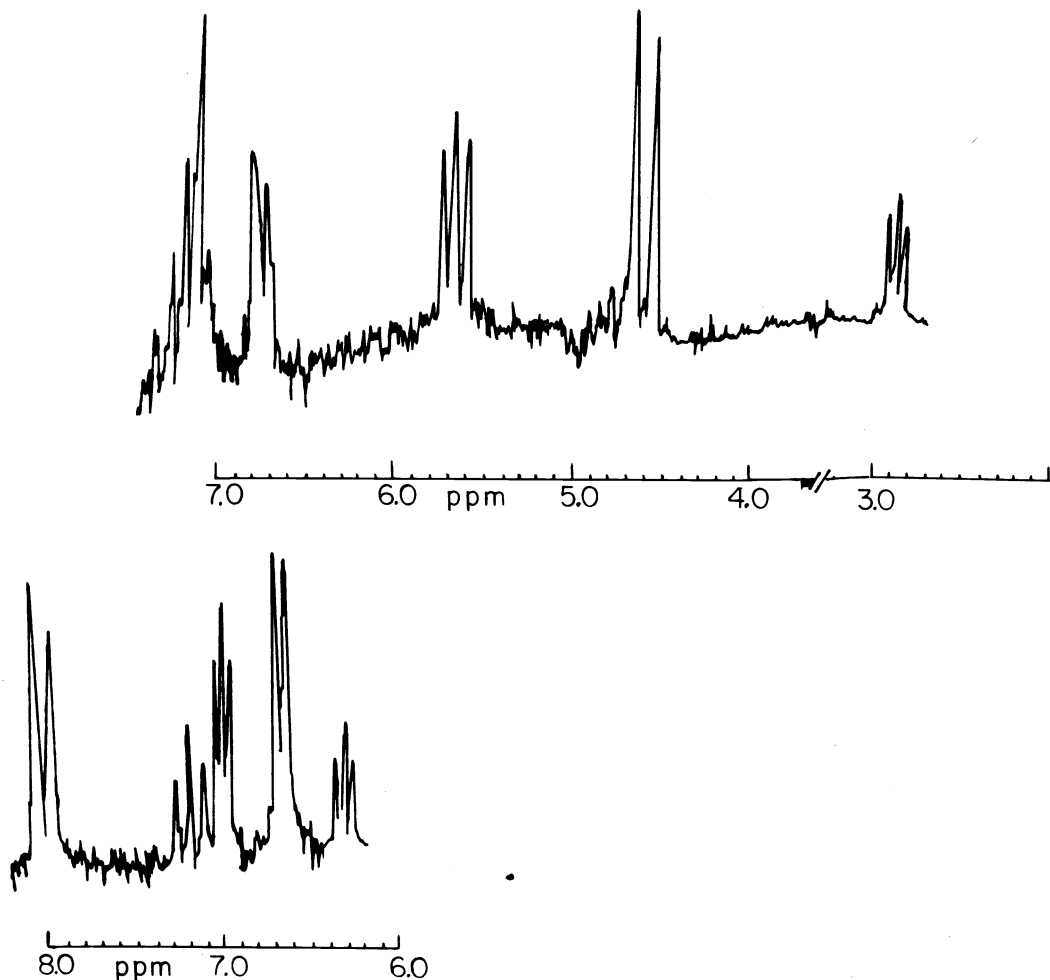
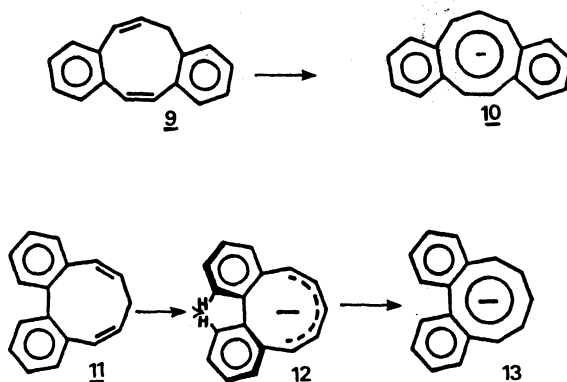
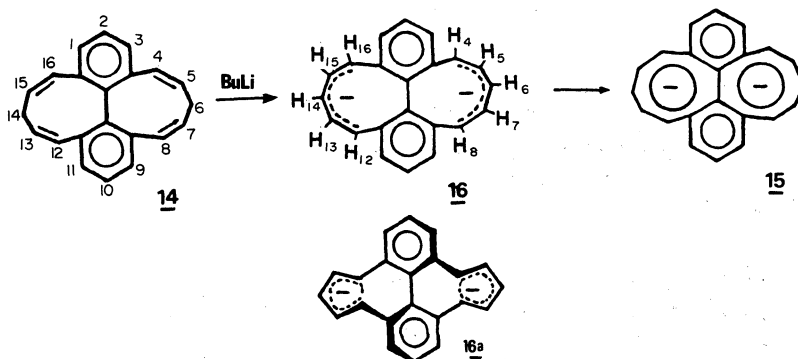


Figure 1: Top (A) NMR Spectrum (100 MHz) of 16. Bottom (B) NMR Spectrum (100 MHz) of Dibenzo[gh,op]nonalene Dianion(15).

Dibenzo[gh,op]nonalene dianion (15) represents a benzannelated aromatic 18π nonalene dianion, a higher homolog of the pentalene and heptalene dianions.

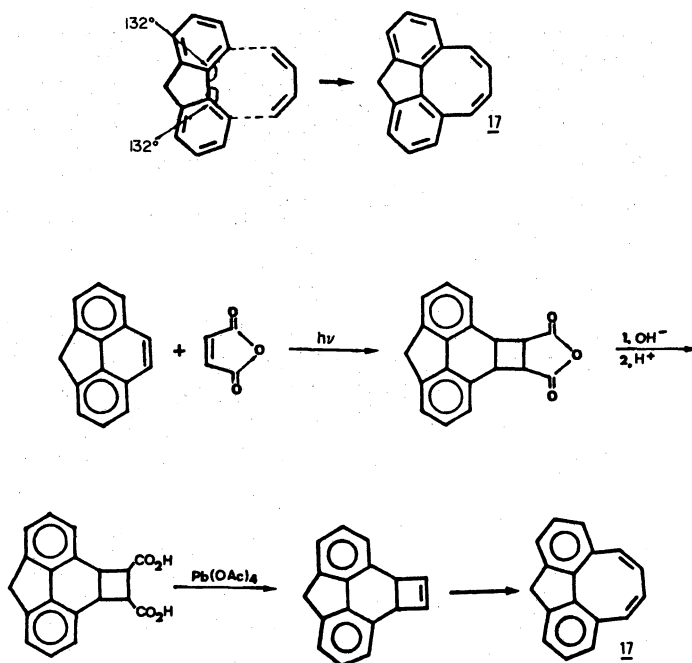


Although *ortho*-interactions due to the biphenyl structure introduce a barrier in achieving a planar configuration of the systems, the special stability of 12 and 16 suggests an additional stabilization present in the pentadienyl anionic intermediates. Molecular models reveal that 16 exists in a twisted conformation 16a. In this structure, *p*- π overlap between positions 4,8 and 12,16 may result in homoaromatic interactions which further contribute to the unique stabilization of this intermediate (13).



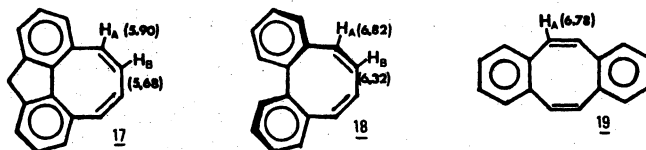
IONS FROM PLANAR COT POLYCYCLE

Recalling the classification of ring fusion, a polycycle composed of a $4n_1\pi + (4n_2 + 2)\pi$ rings acquires an antiaromatic $4n\pi$ peripheral conjugation. The paratropicity involved with an antiaromatic system is theoretically established. However, its experimental verification is difficult due to non-planarity of $4n\pi$ systems (excluding the unstable cyclobutadiene). Realizing these difficulties, we wished to examine the influence of a $4n\pi$ peripheral delocalization in a polycycle which is composed of a 6π -aromatic cyclopentadienyl anionic ring fused to a planar 8π -cyclooctatetraene (COT) moiety (14). The non-planarity of COT provided us with the challenge of designing a polycyclic system in which the COT component is forced to be planar. Cycloocta[def]fluorene (17) seemed to fulfill these requirements on the basis of simple geometrical considerations. The complementary angles of fluorene at positions 4a and 5a are equal to 132° ; therefore the schematic fusion of a butadiene residue to COT seemed a promising approach to a COT moiety with octagonal angles (134°). The synthesis of 17 is outlined in scheme I.

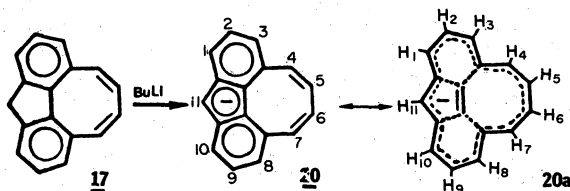


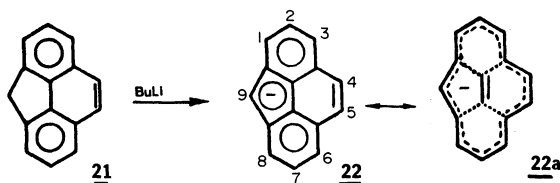
Scheme I
Synthetic Route to Cycloocta[def]fluorene (17)

Indeed, we find that the vinylic protons H_A and H_B in 17 are characterized by a significant paratropic shift as compared to closely related polycycles with a non-planar COT component. (For example, 18 and 19). Comparison of the vinylic proton shifts of 17 to those of the corresponding protons in 18 reveal that the protons H_A and H_B experience a significant paratropic shift of ca. 0.8 ppm. These observations imply that an antiaromatic, planar 8π -ring component is fused to the polycycle.



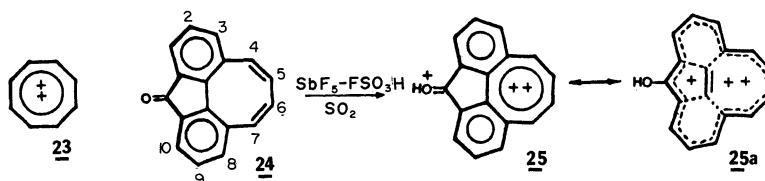
The planarity of the COT component in 17 enables one to examine the contribution of a peripheral 4π conjugation when fused to an aromatic 6π -cyclopentadienyl anionic component. Cycloocta[def]fluorenyl anion (20) is obtained by deprotonation of 17, and the possible contribution of an anti-aromatic 16π peripheral delocalization (20a) should be considered (14).



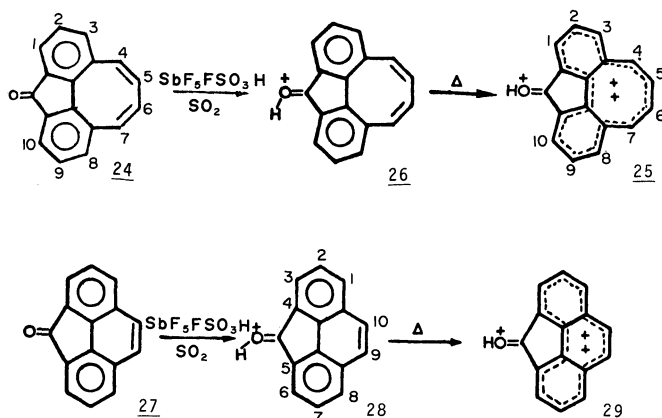


The deprotonation of 17 to 20 is accompanied by a paratropic shift of all the protons. In particular, the protons $H_4 - H_7$ are shifted to the highest extent ($\Delta\delta = 2.4$ ppm). Analysis of the benzene proton pattern emphasizes that a charge shielding is not the sole reason for the highfield proton shifts. In order to estimate the effect of charge shielding on the chemical shifts, the deprotonation of a reference system viz. cyclopenta[def]phenanthrene (21) to 22 was conducted. Formally, 21 is derived from the parent hydrocarbon 20 by the shortening of an "ethylene" bridge. However, as 22 is not expected to show antiaromatic properties, its chemical shifts are influenced by charge shielding only. Comparison of the "parallel" protons of the two anions 20 and 22 indicates that the protons of 20 are shifted to significantly higher field. We therefore consider cycloocta[def]fluorenyl anion (20) to be an antiaromatic-paratropic system due to a peripheral 16π -conjugation (20a). The low acidity of the parent hydrocarbon 17 ($pK_a = 27$) serves as further support for this conclusion. As far as we are aware, this is the lowest acidity value observed in a system which includes a fluorene counterpart, and we attribute this property to the antiaromatic character of the conjugate base 20. Trinajstić (2a) confirmed these conclusions in a graph theory calculation, whereby a negative TRE-PE was found for 20 (-0.011β), consistent with an antiaromatic species.

The planarity of the COT component in 17 led our attention to the possibility of pursuing an oxidation of the conjugated periphery to the corresponding Huckeloid dibenzo-COT dication (15). The problems encountered in the formation of COT-dication (23) originate from charge repulsions and steric strain operative in the planar light-membered ring (see also relevant work described by Olah (16)). The fused benzene rings in 17 are both charge delocalizing components and together with the initial planarity of the COT moiety are expected to suppress the difficulties involved in the oxidation of the monocyclic system. Therefore, we investigated the behavior of cycloocta[def]fluorenone (24) in a strong oxidizing acidic medium ($FSO_3H:SbF_5$, 1:1). In this environment, in addition to protonation of the carbonyl site of 24, oxidation of the conjugated periphery is expected to occur. The resulting tricationic cycloocta[def]fluorenone protonate dication (25) might behave as a non-aromatic 12π -conjugated trication 25a. On the other hand, charge localization at the protonation site should result in a partial 14π -aromatic delocalization over the dibenzo-COT counterpart. Reaction of 24



with $SbF_5:FSO_3H$ at low temperatures ($-40^\circ C$) leads to the conjugate acid 26. Elevation of the temperature of 26 afforded an irreversible two-electron oxidation to form 25 (Scheme II). The dicationic nature of 25 is confirmed by ^{13}C -NMR spectroscopy. The transformation 26 \rightarrow 25 is accompanied by a total downfield ^{13}C -chemical shift of 401 ppm. As a single positive charge is expected to affect the ^{13}C -NMR chemical shifts by a total deshielding of 180-200 ppm, the observed change confirms the dicationic nature of 25. The oxidation process of 26 \rightarrow 25 shows a drastic downfield shift in the proton spectrum, which accumulates to a value of 35.2 ppm. Recalling Schaeffer and Scheinder's correlation (18), a total downfield shift of 21.4 ppm (10.1 ppm/unit of charge) is expected due to deshielding. Thus, the additional downfield shifts can be attributed to a diamagnetic ring current operative in the aromatic dication 25. In order to establish these conclusions and to differentiate between the charge deshielding and the diatropic effect on the chemical shift, we examined the oxidation of cyclopenta[def]phenanthrylene ketone (27) as a reference substrate (15). Reaction of 27 with $FSO_3H:SbF_5$ in SO_2 resulted in a behavior similar to that described for 24. At low temperature ($-40^\circ C$) the protonate 28 is formed, while at room temperature it undergoes a two-electron oxidation to the corresponding cyclopenta[def]phenanthrylene protonate dication (29) (Scheme II). The dication 29 is formally derived from 25 by the elimination of a vinylic group.



Scheme II

However, as this system is expected to be non-aromatic, the deshielding which accompanies the oxidation process $28 \rightarrow 29$, acts as an indicator of charge deshielding effect only. The assignment of the $^1\text{H-NMR}$ chemical shifts involved in the oxidation of the protonates 26 and 28 is summarized in Table I. Comparison of the charge deshielding effects observed in the reference system and the downfield shifts in 25 shows that all the protons in 25 experience a downfield shift which is more than twice as large as that expected from the charge deshielding effect only. This increment is attributed to a diamagnetic ring current operative in the aromatic dibenzo-COT-dicationic counterpart. Indeed, the spectral characteristics of 25 are consistent with the localization of the third positive charge (oxonium ion) at the protonation site. It seems to us that the selective localization of one positive charge and the delocalization of the other two charges originate from charge repulsions as well as from the aromaticity of the debenzo-COT dicationic moiety.

Table I

PROTON CHEMICAL SHIFT DATA OF THE OXIDATION PROCESSES OF THE PROTONATES $26 + 25$ and $28 + 29$

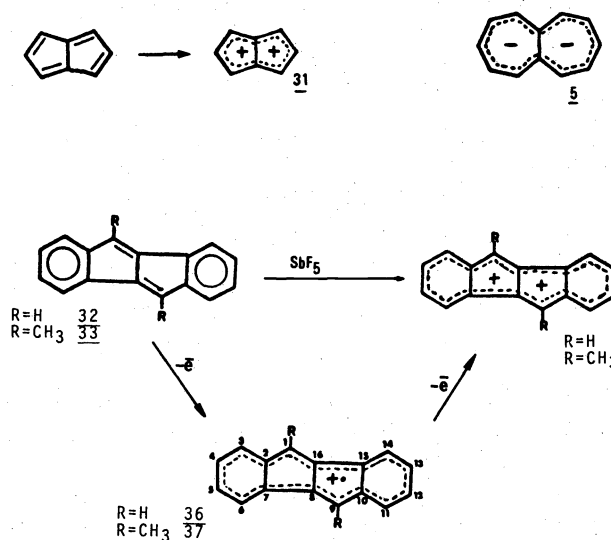
	$H_{\text{benz.}}$	H_9, H_{10}		$H_{\text{benz.}}$	H_4	H_5	H_6	H_7
<u>28</u>	7.12(2H), 7.6(4H)	7.32	<u>26</u>	7.60	5.23	6.34	6.76	6.00
<u>29</u>	7.59(2H), 8.1(4H)	8.58	<u>25</u>	9.30	8.82	8.54	8.54	8.82
$\Delta\delta_{H_i}^b$	0.47; 0.4	1.26	$\Delta\delta_{H_i}^c$	1.7	3.59	2.2	1.78	2.82
$\Delta\delta_{H_i}(\text{av.})^d$	0.42	1.26	$\Delta\delta_{H_i}(\text{av.})^d$	1.7	2.6			

(a) Center of multiplet; (b) $\Delta\delta_{H_i} = \delta_{H_i}(29) - \delta_{H_i}(28)$; (c) $\Delta\delta_{H_i} = \delta_{H_i}(25) - \delta_{H_i}(26)$; (d) $\Delta\delta_{H_i}(\text{av.}) = \Sigma\Delta\delta_{H_i} / \Sigma n_{H_i}$; n_i is the number of the protons of the relevant group.

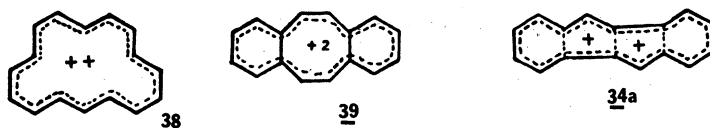
FUSED $4n\pi$ SYSTEMS

The third subclass of conjugated polycycles involves a $(4n_1 + 4n_2)\pi$ ring fusion. As discussed previously, this type of system includes a $(4n + 2)\pi$ periphery, while each of the fused components contributes antiaromatic character. Heptalene dianion (30), reported several years ago by Vogel (6), highlighted the significance of the peripheral 14π aromatic delocalization in characterizing the system. However, attempts to broaden this homologous series by the addition of 6π pentalene dication (31) were unsuccessful. We attribute the difficulties in the preparation of 31 to mutual charge repulsions operative in the relatively small molecular

similar to the difficulties encountered in the formation of COT dications. Therefore, our approach involved the investigation of a dibenzannulated pentalene dication, where the benzene rings are expected to relieve the charge repulsions (19). The parent conjugated hydrocarbon, dibenzo[*b,f*]pentalene (32) (20), and its dimethyl derivative 33 (21), are oxidized chemically by SbF_5 in SO_2ClF to their respective dications 34 and 35. The oxidation of the parent hydrocarbons 32 and 33 was also conducted electrochemically. The electrochemical oxidation follows a consecutive stepwise one-electron pathway. The first one-electron oxidation products are the radical cations 36 and 37, identified by ESR spectroscopy (22).

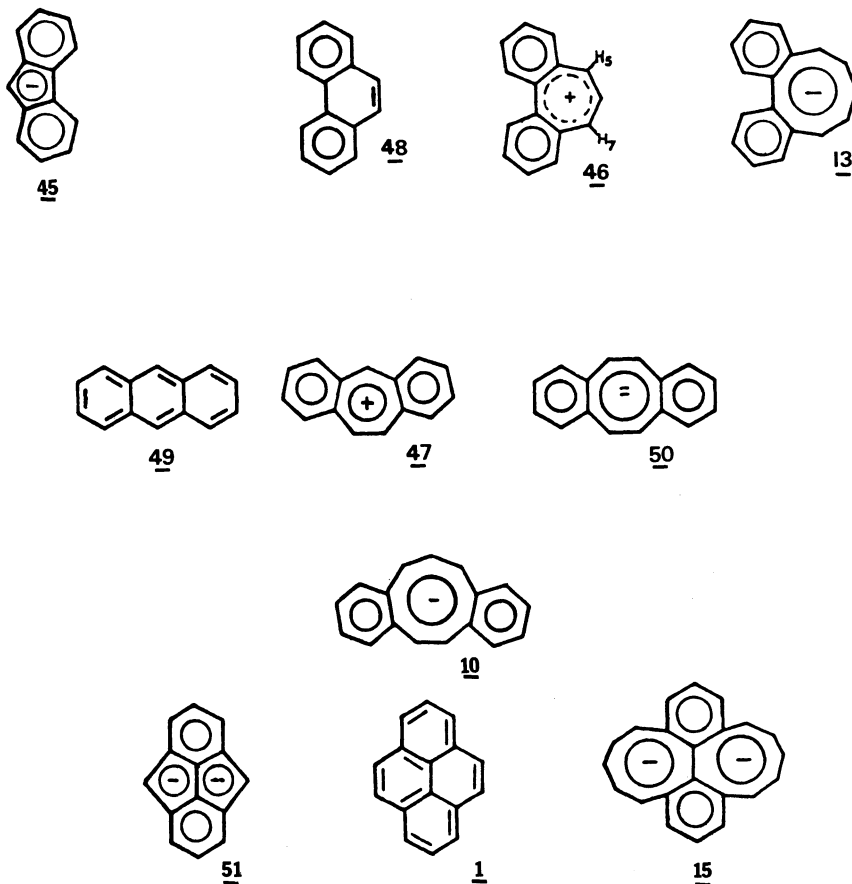


These intermediary ions undergo a further one-electron oxidation process to the respective dications 34 and 35. The dicationic nature of the chemically formed species 34 and 35 was confirmed by the ^{13}C -NMR chemical shift differences accompanying their formation. The cumulative deshielding of carbon shifts is ca. 360 ppm, and is in agreement with the formation of a doubly positive charged species (17). The aromatic nature of the dications 34 and 35 is elucidated by analysis of the changes in the proton chemical shift involved with the oxidation process. The Schaeffer and Schneider correlation predicts a total deshielding of the proton shifts of 10.7 ppm per unit of positive charge (18). So, an estimation of the deshielding effect on the proton shift is possible. The formation of the dibenzo[*b,f*]pentalene dications reveals a significant downfield shift. The analysis of the ^1H -NMR spectrum accompanying the oxidation processes is summarized in Table II. The average downfield shift for each of the protons appears to be 2.8 ppm. Charge deshielding is expected to affect the chemical shifts by an average value of 1.3 ppm; however, the observed downfield shifts in the formation of 34 and 35 are significantly greater than this (by an average of 1.5 ppm). The additional downfield shift is attributed to the influence of a diamagnetic ring current operative in these aromatic dications. The benzannulated ring proton absorption patterns show that charge delocalization as well as diamagnetic ring current are operative over the whole molecular perimeter of 34 and 35. We find that the 16C perimeter of the dibenzo[*b,f*]pentalene dications 34 and 35 reveals similarities in its ^1H and ^{13}C -NMR characteristics to the aromatic [16]annulene dication (38) (23) and dibenzo[*a,e*]COT dication (39) (16). We therefore realize a similarity in the electronic properties of these isoelectronic systems. Our results emphasize that charge delocalization and induced diamagnetic ring current are operative over the periphery, and we consider the dibenzo[*b,f*]pentalene dications as peripheral [16]annulene dications cross-linked by three σ -perturbation bridges 34a and 35a (19).



Comparison of the proton shifts of the dianions 40 and 41 with their corresponding parent conjugated hydrocarbons 32 and 33 reveals that despite the two negative charges introduced, the proton shifts are influenced by a compensating mechanism to the charge shielding effect. This counter-effect is attributed to a diamagnetic ring current operative in the aromatic dianionic systems (19). The proton shifts of the benzenannulated rings imply that the negative charge delocalization and diamagnetic ring current are operative over the whole molecular periphery and are not limited to the pentalene moiety. We therefore rationalize the aromatic character of the dibenzo[b,f]pentalene dianions by a peripheral 18π electron delocalization 40a and 41a. The two electron oxidation and reduction of dibenzo[b,f]pentalene to the respective aromatic dication or dianion demonstrate that a polycyclic system composed of two fused $4n\pi$ rings behaves similarly to monocyclic $4n\pi$ systems in attaining aromaticity. Thus, the contributions of the antiaromatic cyclopentadienyl cationic components present in 34 seem to be quenched by the aromatic peripheral delocalization which is dominant in characterizing the system.

The results we have described allow some insight into the aromaticity of polycyclic charged species. In the discussion, we emphasized the peripheral electron delocalization as a significant contribution to the resultant aromatic or antiaromatic nature of the system. We demonstrated that steric effects, partial and homoaromatic delocalization, and regulation of the degree of charge delocalization are important in the development of aromaticity in the polycyclic series. We visualize that the polycyclic systems represent a variety of new homologous non-benzenoid aromatic series. For example, fluorenyl anion (45), dibenzotropylium cations 46 and 47 represent isoelectronic systems to the neutral phenanthrene (48) and anthracene (49). Dibenzo[a,e]COT dianion (50) and the dibenzocyclononatetraenyl anions 13 and 10 represent homo-electronic systems to the neutral phenanthrene (48) and anthracene (49). Similarly dibenzo[cd,gh]pentalene dianion (51) and dibenzo[gh,op]nonalene dianion (15) represent iso and homo-electronic systems related to the neutral pyrene (1). The completion of this variety of homologous series is still a challenge for the future.



REFERENCES

1. a) "Aromaticity," Chem. Soc. Special Publication No. 21, London (1967).
b) P. J. Garratt, *Aromaticity*, McGraw-Hill, London (1971).
c) "Chemistry of Non-Benzenoid Aromatic Compounds," *Pure and Applied Chemistry* **28**, 111-397 (1971).
2. a) I. Gutman, M. Milun, and N. Trinajstic, *J. Amer. Chem. Soc.* **99**, 1692 (1977); *Croat. Chem. Acta* **48**, 87 (1976).
b) M. Randić, *J. Amer. Chem. Soc.* **99**, 445 (1977).
3. a) J. R. Platt, *J. Chem. Phys.* **22**, 1448 (1956).
b) M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3345 (1952).
c) R. Breslow, R. Grubbs, and S. I. Murahashi, *J. Amer. Chem. Soc.* **92**, 4139 (1970).
4. S. W. Staley, F. Heinrich, and A. W. Orvedal, *J. Amer. Chem. Soc.* **98**, 2681 (1976).
5. E. Vogel, H. Z. Runzheimer, F. Hozrefe, B. Baffner, and J. Lex, *Angew. Chem. Internat.* **16**, 871 (1977).
6. J. F. M. Oth, K. Müller, H. Königshofen, J. Wassen, and E. Vogel, *Helv. Chim. Acta* **57**, 2387 (1974).
7. a) H. E. Simmons and J. K. Williams, *J. Amer. Chem. Soc.* **86**, 3222 (1964).
b) A. G. Anastassiou and E. Reichmanis, *J. C. S. Chem. Commun.*, 149 (1975).
c) A. G. Anastassiou and E. Reichmanis, *Angew. Chem., Internat. Ed.* **13**, 728 (1974).
8. M. Rabinovitz, I. Willner, A. Gamliel, and A. Gazit, *Tetrahedron* **35**, 667 (1979).
9. I. Willner, A. Gamliel, and M. Rabinovitz, *Chemistry Letters*, 1273 (1977).
10. M. Rabinovitz and I. Willner, *Tetrahedron Letters*, 4447 (1974).
11. a) M. Rabinovitz and A. Gazit, *Tetrahedron Letters*, 721 (1972).
b) P. J. Garratt and K. A. Knap, *J. C. S. Chem. Commun.*, 1215 (1970).
12. I. Willner and M. Rabinovitz, *J. Amer. Chem. Soc.* **99**, 4507 (1977).
13. A. Dagan and M. Rabinovitz, *J. Amer. Chem. Soc.* **98**, 8268 (1976).
14. a) I. Willner and M. Rabinovitz, *Tetrahedron Letters*, 1223 (1976).
b) I. Willner and M. Rabinovitz, submitted for publication.
15. I. Willner, A. L. Gutman, and M. Rabinovitz, *J. Amer. Chem. Soc.* **99**, 4167 (1977).
16. a) G. A. Olah, J. S. Staral and L. A. Paquette, *J. Amer. Chem. Soc.* **98**, 1267 (1976).
b) G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Camody, *J. Amer. Chem. Soc.* **99**, 3439 (1977).
17. a) H. Spiesske and W. G. Schneider, *Tetrahedron Letters* 468 (1961).
b) D. A. Forsyth and G. A. Olah, *J. Amer. Chem. Soc.* **98**, 4086 (1976).
c) P. E. Hansen, *Org. Mag. Reson.* **12**, 109 (1979).
18. T. Schaeffer and W. G. Schneider, *Can. J. Chem.* **41**, 966 (1963).
19. a) I. Willner and M. Rabinovitz, *J. Amer. Chem. Soc.* **100**, 337 (1978).
b) I. Willner, J. Y. Becker and M. Rabinovitz, *J. Amer. Chem. Soc.* **101**, 395 (1979).
20. C. T. Blood and R. P. Linstead, *J. Chem. Soc.* 2263 (1952).
21. K. Brand, et al., *Chem. Ber.* **53**, 809, 815 (1920); **55**, 601 (1922), **56**, 2541 (1923).
22. P. Furderer, F. Gerson, M. Rabinovitz, and I. Willner, *Helv. Chim. Acta*, **61**, 2981 (1978).
23. J. F. M. Oth, D. M. Smith, U. Prange, and G. Schroder, *Angew. Chem.* **85**, 352 (1973); *Angew. Chem., Internat. Ed.* **12**, 327 (1973).