rinsing of the outlet collection tube.

In a control experiment, a mixture consisting of carbon-14-labeled styrene (0.3 mCi/mol) and unlabeled organic chloride was injected on the glass column, and the styrene was collected. Immediately following this, 2–2.5 mL of acetone was injected in about 300-μL portions and the effluent acetone for each injection was collected and counted. The second acetone fraction gave about 20000 cpm, the fourth 500 cpm, and the sixth and the seventh only background activities. At its normal retention time the unlabeled chloride was then collected and shown to have only background activity.

Radioactivity Determinations and Isotope Effect Calculations. As outlined under Procedures and Results, the radioactivity determinations were performed on a Beckman Model DPM-100 liquid Scintillation counter by using a cocktail solution prepared from 5 g of 2,5-diphenyloxazole, 0.2 g of DMPOP (1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene), and 1 L of toluene, by using the external standard ratio method. Activities were arranged so that a sample size of 10–20 mg gave a suitable count rate. Because of the problem wiht polymerization of the styrenes, the product activities, R_p, could not be determined in many cases and the isotope effects could then only be determined from one of the four equations of Tong and Yankwich[29] relating the fraction of reaction, f, to the reactant, R_0, and recovered reactant, R_r; otherwise all four equations[29] were used. Typical sample data[42] are presented in Table V, and the results of all the isotope effect experiments are summarized in Table II. The good agreement of the $k/^{\beta}k$ values calculated by the four different equations is to be noted, as is the good agrement of the values calculated at the different fractions of reaction. These kinds of agreement give us confidence that our starting materials are chemically and radiochemically pure and that our isotope effect kinetic and workup procedures are satisfactory.

Registry No. p-$CH_3OC_6H_4CHClCH_3$, 1538-89-2; p-$CH_3C_6H_4CHClCH_3$, 2362-36-9; $C_6H_5CHClCH_3$, 672-65-1; p-$ClC_6H_4CHClCH_3$, 20001-65-4; p-$CF_3C_6H_4CHClCH_3$, 85289-90-3; p-$NO_2C_6H_4CHClCH_3$, 19935-75-2; m-$CH_3OC_6H_4CHClCH_3$, 58114-05-9; m-$NO_2C_6H_4CHClCH_3$, 34586-27-1; Ph_3P, 603-35-0; ^{14}C, 14762-75-5; methoxybenzene, 100-66-3; acetyl chloride, 75-36-5; 4-methoxyacetophenone, 100-06-1; 1-(4-methoxyphenyl)ethyl alcohol, 3319-15-1; 4-nitroacetophenone, 100-19-6; 1-(4-nitrophenyl)ethyl alcohol, 6531-13-1; 1-bromo-4-(trifluoromethyl)benzene, 402-43-7; acetaldehyde, 75-07-0; 1-(-(trifluoromethyl)phenyl)ethyl alcohol, 1737-26-4; 1-(3-nitrophenyl)ethyl alcohol, 5400-78-2.

Priority of Aromatic Delocalization: Electron Distributions, Chemical Stability, and σ-Framework in Conjugated Polycycles

Abraham Minsky,[1a] Amatzya Y. Meyer,[1a] Klaus Hafner,[1b] and Mordecai Rabinovitz*[1a]

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, and the Institut für Organische Chemie der Technischen Hochschule, Darmstadt, F.R.G. *Received October 14, 1982*

Abstract: NMR studies and theoretical calculations were performed on nonalternant pericondensed polycyclic systems such as aceheptylene, acenaphthylene, and their charged derivatives. The results point toward a significant tendency of the systems to sustain aromaticity or, if impossible, to avoid antiaromaticity and to become nonaromatic. These goals are achieved by sustaining diamagnetic modes of electron distributions over the π-framework. A comprehensive discussion of the various possible delocalization modes enables a better understanding of the role of aromaticity as well as a critical treatment of its definitions.

One of the most striking phenomena related to aromaticity is the unusual tendency of aromatic systems to remain so.[2] This tendency is demonstrated by a large variety of chemical and physical patterns. The predisposition to electrophilic substitutions vs. low proclivity toward additions and the existence of significant dipole moments due to uneven electron distribution over different moieties of the molecule (e.g., azulene and unsymmetrical fulvalenes[3]) are two known examples of the mentioned phenomenon. Nonaromatic species reveal a pronounced tendency to acquire aromaticity via the release of a positive or negative group or via oxidation and reduction processes (e.g., cyclopentadiene, cycloheptatriene,[2c] and cyclooctatetraene[4]). The substantial driving force involved with the aromatic character reflects the low-energy content of aromatic species caused by a stabilizing cyclic electron delocalization.

The most elegant demonstration of the tendency of systems to sustain aromatic character is probably revealed in nonalternant, conjugated, pericondensed polycycles. These compounds can accommodate, in principle, more than one mode of delocalization of electrons over the π-framework. The π-electrons may be evenly distributed over the entire carbon skeleton—including the inner atoms (e.g., C_{13} and C_{11} in **1** and **4**, respectively). Yet, other modes may exist and result in the establishment of a variety of plausible paths of conjugation. For example, π-electrons may be delocalized in the system's periphery and cause, therefore, a peripheral, annulenic-type path of conjugation in which the inner carbons do not participate. On the other hand, conjugated paths may be established over a part of the periphery only (e.g., the naphthalene moiety in **4**). At first sight there is no reason to assume or expect a larger contribution of one conjugation path over the others. Yet, the present study points unequivocally toward the dominance of one particular path of electron distribution in the polycyclic system,

---

[1] (a) The Hebrew University of Jerusalem. (b) The Institut für Organische Chemie der Technischen Hochschule Darmstadt.

[2] For a general review see: (a) Bergmann, E. D.; Pullman, B., Eds. "Aromaticity, Pseudoaromaticity, Antiaromaticity"; Academic Press: Jerusalem, 1971. (b) Garratt, P. J. "Aromaticity"; McGraw-Hill: London, 1971. (c) Streitweiser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; pp 256–294. (d) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; Part A, pp 369–419. (e) Dewar, M. J. S. "The MO Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; pp 152–190.

[3] Nakajima, T. In "Molecular Orbitals in Chemistry, Physics and Biology"; Löwdin, P. O.; Pullman, B., Eds.; Academic Press: New York, 1964.

[4] (a) Olah, G. A.; Staral, J. S.; Liang, G.; Paquette, L. A.; Melega, W. P.; Carmody, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3349–3354. (b) Katz, T. J. *Ibid.* **1960**, *82*, 3784–3785.

0002-7863/83/1505-3975$01.50/0

Table I. ^1H NMR Patterns[a] of 1, 2, and 3

	$H_{1,2}$	$H_{3,10}$	$H_{4,9}$	$H_{5,8}$	$H_{6,7}$	^1H center of gravity of the heptalene moiety	overall ^1H center of gravity
1	6.98 (s)	6.71 (d, J = 9.1 Hz)	5.19 (dd, J = 10.6, 8.9 Hz)	5.79 (dd, J = 11.8, 8.6 Hz)	5.36 (d, J = 12.0 Hz)	5.77	6.00
2	7.08 (s)	6.54 (d, J = 9.3 Hz)	6.75 (t, J = 9.0 Hz)	5.76 (t, J = 9.1 Hz)	7.61 (d, J = 9.1 Hz)	6.66	6.75
3	6.58 (s)	8.09 (d, J = 8.8 Hz)	8.62 (t, J = 9.2 Hz)	8.20 (t, J = 10.2 Hz)	8.73 (d, J = 10.5 Hz)	8.47	8.09

[a] ppm, referenced to Me_4Si; for numbering, see the schemes.

Table II. ^{13}C NMR Patterns,[a] Charge Densities, and Relevant Orbital Coefficients in 1, 2, and 3

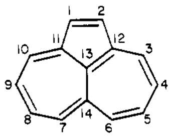
	$C_{1,2}$	$C_{3,10}$	$C_{4,9}$	$C_{5,8}$	$C_{6,7}$	$C_{11,12}$	C_{13}	C_{14}
1: ^{13}C	123.3	142.6	120.9	140.4	132.5	135.1	153.1	158.9
charge density[b]	−0.0867	0.0450	−0.0136	0.0539	0.0013	−0.0674	0.0422	0.0930
LUMO coefficients[b,c]	0.1160	0.3356	0.0005	0.3897	0.1406	0.1387	0.4415	0.4137
HOMO coefficients[b,d]	0.2829	0.1578	0.3626	0.0758	0.3235	0.3913	0.0	0.0
2: ^{13}C	112.4	97.1	121.1	91.4	119.7	123.9	85.6	114.7
charge density[b]	−0.1422	−0.1432	−0.0865	−0.1870	−0.1021	−0.1525	−0.2178	−0.1555
3: ^{13}C	151.1	152.0	178.9	151.5	177.1	176.3	147.7	152.7
charge density[b]	0.0365	0.1506	0.2030	0.1299	0.2013	0.1542	0.1112	0.1376

[a] ppm, referenced to Me_4Si; for numbering, see the schemes. [b] As obtained from $\omega\beta$ calculations.[15] [c] The orbital into which two electrons are added in the reduction process. [d] The orbital out of which two electrons are subtracted in the oxidation process.

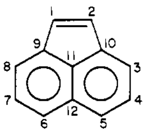
a path which largely contributes to the system's character. This dominance is rationalized in terms of a low-energy content which is related to the prevailing distribution mode. A comparison between the various modes in different systems and, even more so, between neutral and the corresponding charged species reveals a clear correlation between the total number of π-electrons available and the prevailing delocalization mode. The number of π-electrons is related, in turn, to the existence of relative aromatic, nonaromatic, or antiaromatic character (vide infra).

The term "antiaromaticity", proposed for the first time by Breslow,[5] stands for those systems in which cyclic conjugation results in an enhanced destabilization with respect to the corresponding acyclic conjugated systems[6]. This should be contrasted with nonaromatic species in which cyclic electron delocalization does not lead to a change in energy content.

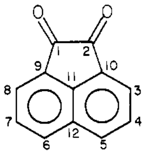
NMR studies as well as theoretical calculations were performed on the aceheptylene system(**1**) and on its hitherto undocumented corresponding doubly charged derivatives. The results are compared with those obtained from the acenaphthylene system (**4**) and its doubly charged species, and the different possible modes of electron distributions are discussed. The factors determining whether one mode or another would prevail point toward the crucial role of aromaticity and antiaromaticity on the behavior of species and enable a critical discussion of the various definitions of aromatic character.



1



4



6

Results

^1H NMR patterns of aceheptylene (**1**), its dianion (**2**), and dication (**3**)[7] are summarized in Table I (Figure 1). The chemical shifts exhibited by the heptalene moiety protons of **1** appear at 5.17–6.74 ppm—a typical vinylic range. The NMR center of gravity of these protons is found to be at 5.77 ppm. The protons on the cyclopentadiene moiety ($H_{1,2}$) reveal a rather low-field chemical shift, viz., 6.98 ppm. The overall ^1H NMR bands center of gravity of **1** is 6.00 ppm. The ^{13}C NMR spectrum of **1** (Table II) reveals the expected eight absorptions which are spread over a relatively large range of chemical shifts (ca. 28 ppm).

The reduction of **1** to its corresponding dianion **2** was performed with sodium metal. The deep blue solution obtained after 4 days of exposure to the metal exhibited a highly resolved first-order ^1H NMR spectrum. The spectrum is composed of a singlet (7.08, $H_{1,2}$), two doublets (6.54, $H_{3,10}$; 7.61, $H_{6,7}$), and two triplets (6.75, $H_{4,9}$; 5.76, $H_{5,8}$). The center of gravity of the proton bands of the seven-membered rings is 6.66 ppm, and the overall center of gravity (which includes the absorptions of the cyclopentadiene ring protons) is found to be 6.75 ppm. The dianionic nature of **2** is clearly deduced from its ^{13}C NMR patterns (Table II). Seven out of the eight ^{13}C bands undergo, in the reduction process **1** → **2**, paratropic displacements which amount to 366 ppm. This value corresponds to 183 ppm/electron—in good agreement with the Spiesecke and Schneider correlation which predicts a total ^{13}C band shift of ca. 180 ppm/charge unit.[8] The largest paratropic shift is observed for the inner carbon atom C_{13}; its absorption is displaced by 67.6 ppm.

When **1** was treated with SbF_5 in SO_2ClF, a dark green solution, attributed to the formation of aceheptylene dication (**3**), was obtained. The ^1H NMR spectrum of **3** points toward a clear difference in charge distribution and in ring currents between the five-membered ring and the heptalene moiety. While the protons on the heptalene moiety exhibit two doublets (8.73, $H_{6,7}$; 8.09, $H_{3,10}$) and two triplets (8.62, $H_{4,9}$; 8.20, $H_{5,8}$) which are considerably low-field shifted in respect of the corresponding neutral system **1** (with a center of gravity at 8.47 and 5.77 ppm, respectively), the cyclopentadiene moiety protons undergo a high-field shift and appear as a singlet at 6.58 ppm. Analogously to the dianion case, the ^{13}C NMR spectrum of **2** reveals its dicationic nature as a total low-field diatropic shift of 371.66 ppm (Table II) is observed.

The ^1H NMR spectrum of acenaphthylene (**4**) is composed of an aromatic ABC pattern (7.57–7.89 ppm) due to the protons on the naphthalene moiety and a singlet due to the five-membered ring protons at 7.13 ppm (Table III; Figure 2). The ^{13}C NMR

---

[5] Breslow, R. *Chem. Eng. News* **1965**, *43*, 90–99.

[6] Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393–398.

[7] Hafner, K. *Pure Appl. Chem.* **1971**, *28*, 153–180. The dianion **2** as the lithium salt has been prepared independently by Müllen: K. Müllen, personal communication.

[8] Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468–471.

Table III. ^{1}H NMR Patterns[a] of 4 and 5

	$H_{1,2}$	$H_{3,8}$	$H_{4,7}$	$H_{5,6}$	overall ^{1}H center of gravity
4	7.13 (s)	7.87 (d, $J = 7.9$ Hz)	7.59 (dd, $J = 8.4, 8.2$ Hz)	7.74 (d, $J = 6.2$ Hz)	7.56
5	5.12 (s)	4.51 (d, $J = 8.1$ Hz)	5.10 (t, $J = 6.7$ Hz)	3.39 (d, $J = 6.5$ Hz)	4.53

[a] ppm, referenced to Me_4Si; for numbering, see the schemes.

Table IV. ^{13}C NMR Patterns,[a] Charge Densities, and Relevant Orbital Coefficients in 4 and 5

	$C_{1,2}$	$C_{3,8}$	$C_{4,7}$	$C_{5,6}$	$C_{9,10}$	C_{11}	C_{12}
4: ^{13}C	129.4	124.1	127.8	127.3	139.7	128.2	128.4
charge densities[b]	−0.0313	0.0381	0.0043	0.0249	−0.0149	−0.0465	0.0043
LUMO coefficients[b,c]	0.3175	0.3671	0.1519	0.3921	0.2961	0.0	0.0
5: ^{13}C	85.8	96.8	126.1	81.8	123.1	137.6	148.9
charge densities[b]	−0.2272	−0.1772	−0.0882	−0.2438	−0.1697	−0.1218	−0.0661

[a] ppm, referenced to Me_4Si; for numbering, see the schemes. [b] As obtained from $\omega\beta$ calculations. [c] The orbital into which two electrons are added in the reduction process.

Table V. ^{13}C NMR Patterns[a] of **6** and **7**

	$C_{1,2}$	$C_{3,8}$	$C_{4,7}$	$C_{5,6}$	$C_{9,10}$	C_{11}	C_{12}
6	194.0	130.0	118.9	125.9	121.5	129.7	128.1
7	181.4	146.8	132.2	137.1	116.4	164.1	130.8

[a] ppm, referenced to Me_4Si; for numbering, see the schemes.

spectrum of **4** (Table IV) reveals seven bands in the range 124.1–139.7 ppm, a typical ^{13}C NMR aromatic chemical shift range. The dianion of acenaphtylene (**5**) has been prepared previously by reduction of the hydrocarbon in tetrahydrofuran solution with sodium metal.[9] The ^{1}H NMR spectrum exhibited by the green solution of the dianion (Table III; Figure 2) ranges between 3.38 and 5.12 ppm with a center of gravity at 4.40 ppm, higher by 3.1 ppm than the center of gravity found in the neutral hydrocarbon. The ^{13}C NMR bands of **2** (Table IV) are paratropically shifted in respect to the bands of the neutral compound by a total of 237.9 ppm. This value is considerably smaller than the total displacement observed in **2** and smaller than the value expected when referring to the mentioned charge-shift correlation.[8] Another striking difference between the ^{13}C NMR spectra of **2** and **5** emerges when the chemical shifts of the inner carbons (i.e., C_{13} in **2** and C_{11} in **5**) are examined. While the absorption of C_{13} is high-field shifted by 67.6 ppm in the reduction process **1** → **2**, the 2-fold reduction of **4** to **5** results in a low-field shift of the inner carbon C_{11} by 9.47 ppm.

Treatment of **4** with SbF_5 probably results in a radical cation which polymerizes readily. Information about a doubly positively charged system of an acenaphthylene skeleton was therefore obtained by a 2-fold protonation process of acenaphthoquinone (**6** → **7**).[10] The ^{1}H NMR spectrum of the diprotonated quinone reveals an ABC pattern with a center of gravity at 8.93 ppm which is low-field shifted in respect to the neutral quinone **6** center of gravity by 1.63 ppm. The ^{13}C NMR spectrum of **7** (Table V) reflects its diprotonated nature by exhibiting a total diatropic band displacement. The inner carbon C_{11} experiences the most pronounced downfield shift, being displaced by 34.40 ppm in the course of protonation process **6** → **7**.

Discussion

The most comprehensive definition of the numerous definitions and criteria suggested to define aromaticity is the one based on the energy content of aromatic systems. Dewar[1e] has defined aromatic molecules as cyclic species with a large resonance energy in which all the atoms in the ring take part in a single conjugated array. In other words, aromatic systems sustain a cyclic π-electron delocalization which reduces the energy content of the systems relative to that of corresponding model compounds without cyclic delocalization. Similarly, antiaromatic systems reveal a cyclic π-electron delocalization which leads to a strong destablization and therefore to a high energy content in respect to analogous acyclic compounds. As a criterion of aromaticity or antiaromaticity, it is difficult to apply this energetically based definition in practice. The more practical definitions can be classified into two general groups: criteria based on purely theoretical concepts and those which refer to experimentally observable phenomena. The peripheral criterion suggested by Platt[11] exemplifies the first group of definitions by assigning aromatic character to a cyclic or polycyclic system with $(4n + 2)$ π-electrons in its periphery. Systems with $4n$ π-electrons in the path of conjugation would be inclined to reveal antiaromatic properties, while those with $(4n + 1)$ or $(4n + 3)$ peripheral conjugated π-electrons would be estimated as nonaromatic. This structural concept is based on the free electron theory and treats crosslinks and inner sp^{2} carbons as small perturbations. The most useful definition among those which relate to experimentally observable phenomena is based on magnetic anisotropy.[12] According to this criterion, aromatic compounds are defined as cyclic or polycyclic systems which sustain a diamagnetic ring current and consequently exhibit a total diatropic, low-field ^{1}H NMR chemical shift relative to that of vinylic protons. Paramagnetic ring current is expected and was shown to be induced in antiaromatic species and to result in a total high-field ^{1}H NMR band displacement[12,13] while nonaromatic compounds give rise to characteristic vinylic ^{1}H NMR patterns. Another experimentally based criterion for aromaticity refers to bond length alternation.[2] An aromatic compound is supposed to reveal a low degree of bond length alternation around the characteristic aromatic bond length (1.4 Å) in contrast with nonar-

---

(9) Lawler, R. G.; Ristagno, C. V. *J. Am. Chem. Soc.* **1969**, *91*, 1534–1535.

(10) Bruck, D.; Minsky, A.; Dagan, A.; Rabinovitz, M. *Tetrahedron Lett.* **1981**, *22*, 3345–3348.

(11) Platt, J. R. J. *Chem. Phys.* **1954**, *22*, 1448–1458.

(12) (a) Elvidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 856–866. (b) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–1548. (c) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598. (d) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Fortsch. Chem. Forsch.* **1970**, *16*, 103–220.

(13) (a) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811–4815. (b) Longuet-Higgins, H. C. *Spec. Publ.—Chem. Soc.* **1967**, *No. 21*, 109–111. (c) Willner, I.; Rabinovitz, M. *J. Org. Chem.* **1980**, *45*, 1628–1633.

(14) Oth, J. F. M.; Müllen, K.; Konigshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387–2398.

(15) Modified ω calculations on Coulomb integrals: (a) Berson, J. A.; Evleth, E. M.; Hamlet, Z. *J. Am. Chem. Soc.* **1965**, *87*, 2901–2908. (b) Boyd, G. V.; Singer, N. *Tetrahedron* **1966**, *22*, 3383–3392. (c) Streitwieser, A. *J. Am. Chem. Soc.* **1960**, *82*, 4123–4135.

(16) Rabinovitz, M.; Willner, I. *Pure Appl. Chem.* **1980**, *52*, 1575–1585.

(17) (a) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2689–2694. (b) Gastmans, J. P.; Gastmans, D. F.; Ferraz, M. H. M. *Tetrahedron* **1977**, *33*, 2205–2213.

(18) Hine, J. *J. Org. Chem.* **1966**, *31*, 1236–1244.

(19) Schaefer, T.; Schneider, W. F. *Can. J. Chem.* **1963**, *41*, 966–982.

(20) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron Lett.* **1982**, *23*, 5351–5354.

(21) For example, the total ^{13}C NMR band displacement observed in the reduction process of anthracene and phenanthrene to their corresponding antiaromatic dianions does not reveal the expected correlation. See: Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 1296–1304.

omatic species in which a substantial bond alternation occurs.

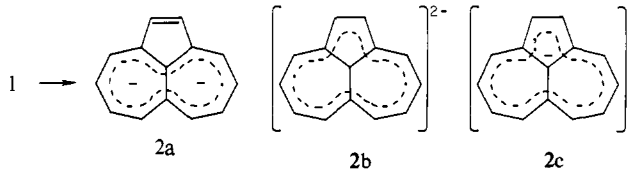
The described definitions have been widely used to characterize aromaticity. However, the correlation between these criteria and aromatic (or antiaromatic) nature is by no means simple. There is no clear, straightforward explanation why the number or modes of distribution of π-electrons in the periphery of polycyclic systems do correlate with aromaticity.[22] Even more so, the aromatic character is, by definition, a relative property, namely, one can assign aromaticity only by referring to model compounds. Thus, even when the number of π-electrons calls for the existence of aromatic character, its extent cannot be predicted. Similarly the relationship between magnetic susceptibility of a polycycle and its conjugative stabilization is highly complex.[23] The various definitions are applied to systems **1**–**7**—a treatment which enables a cross-examination and therefore a better understanding of these criteria.

Aceheptylene (1). The aceheptylene is a system of 14 carbon atoms of which 13 compose its conjugated periphery. Accordingly, **1** can be considered as perturbed [13]annulene or as a $(4n + 1)$ π conjugated system ($n = 3$) with an inner carbon atom. In view of the mentioned Platt's peripheral definition,[11] such a compound is expected to be a nonaromatic polyvinylic system, not exhibiting any aromatic or antiaromatic properties. This expectation is unambiguously confirmed.

X-ray analysis[7] of 3,5,8,10-tetramethylaceheptylene shows a symmetrical planar structure and a significant bond length alternation. The ^{1}H NMR spectrum of **1** (Figure 1; Table I) reveals a typical vinylic range with chemical shifts between 5.17 and 6.98 ppm. The relatively low-field shift of the five-membered ring protons (6.98 ppm) is rationalized by the overall magnetic anisotropy caused by the heptalene moiety double bonds, rather than by assigning a partial aromatic character to the cyclopentadiene moiety. The nonaromatic nature of aceheptylene is clearly indicated by its high-field chemical shift range. A comparison between the chemical shifts of **1** and those exhibited by the heptalene system[14] reflects the nonantiaromatic nature of the former. Although antiaromaticity, imposed on heptalene by its [12] π-electron perimeter, is quenched, at least partially, by nonplanarity, its ^{1}H chemical shift center of gravity reveals a paratropic displacement relative to the corresponding value exhibited by **1** (5.48 vs. 6.00 ppm, respectively).

The acenaphthylene system (**4**) is a 12 carbon atom compound, of which 11 conjugated carbons compose its periphery. According to Platt's model, **4** should be depicted as a perturbed [11]annulene, or as a $(4n + 3)$ π conjugated system ($n = 2$), with an inner carbon atom acting as a weak perturbation to the annulene skeleton. Consequently, acenaphthylene is expected to reveal a nonaromatic, polyvinylic character, analogously to the $(4n + 1)$ aceheptylene system (**1**). Yet the two systems exhibit a clear dissimilarity. In contrast with the ^{1}H NMR bands of **1** which appear in the vinylic range, those of **4** range between 7.13 and 7.89 ppm (Figure 2; Table III), pointing unambiguously toward the presence of an aromatic character. A clue to the source of the difference between the two systems is obtained by inspecting their bond lengths as estimated by $\omega\beta$ calculations.[15] As discussed above, aceheptylene should be depicted as a perturbed annulene which exhibits characteristic polyvinylic bond lengths alternation (as revealed by X-rays and estimated by $\omega\beta$ calculations). On the basis of bond length considerations, acenaphthylene (**4**) is best described as a system composed of an aromatic naphthalene moiety weakly conjugated with an outer double bond. The lengths of the naphthalene moiety bonds are estimated to vary between 1.3802 and 1.4212 Å—a typical aromatic bond length range. The length of the C_1–C_2 bond is calculated to be 1.3559 Å—a length which characterizes a double bond. The value estimated for the bonds which attach the naphthalene moiety to the C_1–C_2 bond is 1.4526 Å—substantially longer than all the other carbon–carbon bonds in the system. Thus, the acenaphthylene (**4**) may be regarded as an aromatic system (relative to its higher homologue, i.e., the aceheptylene system, **1**) which suffers a small perturbation due to an outer double bond. This depiction is closely analogous to the way by which the aromaticity of the pyrene system is rationalized, i.e., a $(4n + 2)$ Hückeloid perimeter (the 14 π periphery) undergoing a weak perturbation which is due in this case to an inner double bond.[16] Theoretical calculations at various degrees of sophistication confirm the above considerations by assigning large resonance energy to **4** and a very small one to **1**.[17]

Scheme I



Aceheptylene Dianion (2). In the course of a metal reduction process of aceheptylene, two electrons are inserted into its π-framework to yield a system of 14 sp^2 carbon atoms and 16 π-electrons. In principle these π-electrons can accommodate three modes of different distributions over the system (Scheme I): (**2a**) The two extra π-electrons may be introduced into the heptalene moiety. The resultant species may be visualized as composed of a heptalene dianion coupled with a double bond in the same sense as the previously described coupling between the naphthalene moiety and the double bond in acenphthylene (**4**). Such a mode of electron distribution will result in an aromatic character due to the aromaticity of the heptalene dianion moiety.[14] (**2b**) The two extra π-electrons might be introduced into the periphery of the system. In this case a [13C-15π] peripheral system is obtained (viz., **2b**) with a $(4n + 3;\ n = 3)$ perimeter. According to the mentioned Platt's peripheral model, the dianion will reveal a nonaromatic character. (**2c**) The third possibility of π-electron distribution over the aceheptylene dianion system considers one of the two inserted electrons to be located at the inner carbon atom (C_{13}) and the other to be delocalized over the entire periphery. This mode would result in a [13C-14π] periphery coupled with an inner negatively charged carbon (viz., **2c**). A Hückeloid periphery of 14 π-electrons is therefore obtained and aromatic character is expected.

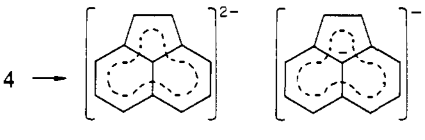
In view of the driving force involved in aromaticity (vide supra) the second possibility, leading to nonaromatic character, is ruled out. Kinetic as well as thermodynamic considerations led strength to the third possibility. Theoretical calculations performed on aceheptylene (**1**) point toward a very large atomic coefficient of the atomic orbital which belongs to the inner carbon C_{13} in the lowest vacant molecular orbital of the neutral compound. (The atomic coefficients of the LUMO of **1**—the orbital into which two electrons are added—are reported in Table II.) This indicates that the carbon is prone to acquire a substantial charge density. Even more so, the aceheptylene, as starting material for the reduction process, was shown to be best described as a peripheral system coupled with an inner perturbation. Consequently, the distribution of electrons in the dianion as proposed in **2c** would minimize the reorganization of electrons in the course of the reduction process. According to Hine's rule,[18] reactions will be favored when involving the least change in atomic positions and electron configurations, due to relatively small activation energies. While substantial changes of electron distribution and large atomic relocations (e.g., a shortening of the C_1–C_2 bond and an increase of the C_1–C_{11} and C_2–C_{12} bond lengths) are expected according to the first proposed distribution mode, no such phenomena should occur if the reduction proceeds via the third mode. Thermodynamically, the repulsion between two negative charges distributed only on the heptalene moiety would be undeniably stronger than the repulsion occurring when one negative charge is located on an inner atom and the other charge distributed over all the periphery. Indeed, ^{1}H and ^{13}C NMR spectra, as well as theoretical calculations performed on **2**, point unequivocally toward an

---

[22] The concept of relative aromatic character—a principle upon which our discussion is based—has been emphasized by Epiotis: Epiotis, N. D., *Pure Appl. Chem.* **1983**, *55*, 199–206.

[23] (a) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 5913–5917; (b) **1979**, *101*, 558–563.

Scheme II



5a 5b

aromatic dianion in which one negative charge is located on the inner carbon atom, while the second is delocalized on the periphery. The center of gravity of the ^{1}H NMR spectrum of **2** is diatropically shifted in respect to that of **1** by 0.75 ppm. This low-field displacement is rationalized in terms of the diamagnetic ring current related to aromaticity which is sustained in **2**. It should be noted that the diamagnetic ring current effect is in fact much larger, the aromatic low-field shift being partially quenched by the shielding of the two negative charges.

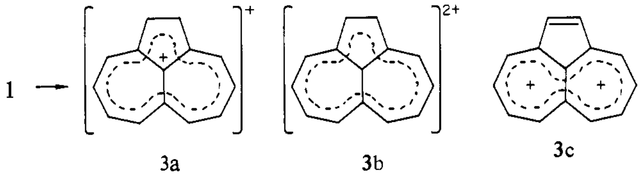
As described previously, the ^{13}C NMR bands of **2** reveal a total high-field shift of 366 ppm with respect to the neutral compound ^{13}C chemical shift, indicating the presence of doubly charged species.[8]

The inner carbon atom C_{13} undergoes an unusually large paratropic shift of 67.6 ppm, a value rationalized by a large negative charge density on this carbon, in accord with the suggested electron distribution mode. This mode is further supported by $\omega\beta$ calculations which were performed on the dianion **2**. The calculations estimate (i) a large negative charge density on the inner carbon C_{13} (Table II) and (ii) a relatively small degree of bond lengths alternation on the periphery vs. a very long bond between C_{13} and C_{14} (1.4891 Å).

Acenaphthylene Dianion (5). The dianion is composed of 12 carbons and 14 π-electrons which can accommodate in principle two different modes of electron delocalizations (Scheme II): (**5a**) The two "extra" electrons can be inserted into the periphery resulting in a [11C-13π] system. (**5b**) One of the two electrons is located on the inner carbon atom C_{11} and the other one delocalized over the 11 carbon periphery analogous to the electron distribution in the aceheptylene dianion (**2**). The resulting species would be a [11C-12π] peripheral system which, according to Platt's model, would be expected to reveal an antiaromatic character.

We turned to $\omega\beta$ calculations as a means of assessing the portion of ^{1}H NMR chemical shift due solely to charge shielding. It was shown that in cyclic conjugated systems the proton chemical shifts are related linearly to the π-electron density. This relationship, known as the Schaefer and Schneider correlation,[19] uses a correlation constant of 10.7 ppm/unit charge. Thus, we summed the theoretical charges on hydrogen-bearing carbon atoms of **5** and multiplied the sum by 10.7. The product was then divided by the number of protons and this average subtracted from the center of gravity of the ^{1}H NMR chemical shifts exhibited by the neutral acenaphthylene (**4**). An estimate is thus derived for the displacement in the center of gravity that is due to shielding by the two negative charges. The ^{1}H NMR center of gravity of **4** is found to be 7.56 ppm; the theoretical high-field displacement due to negative charge density is estimated as 1.99 ppm. Therefore, the center of gravity of **5** due only to negative shielding would be 5.57 ppm, while the exhibited center of gravity is 4.53 ppm. The difference between the two values (1.04 ppm) is relatively small (when compared with paratropic displacements due only to paramagnetic ring current in antiaromatic species such as anthracene dianion, chrysene dianion, or phenanthrene dianion with high-field shifts of 2.90, 4.06, and 5.33 ppm, respectively[20]). On the basis of these observations and arguments, the total ^{1}H NMR high-field chemical shift observed in the process **4** → **5** is rationalized in terms of negative charge density shielding and the quench of the diatropic aromatic ring current which prevails in the neutral system **4** (vide supra). An antiaromatic character is not found to be generated in **5** as would be the case according to the second proposed possibility of electrons distribution mode in **5**, i.e., one electron residing on the inner carbon and the second on the periphery (viz., **5b**).

Scheme III



3a 3b 3c

A comparison between the ^{13}C patterns of the neutral system **2** and that exhibited by its corresponding dianion **5** is particularly instructive. As described in the results section the total high-field displacement of ^{13}C bands in the course of the reduction **4** → **5** is considerably smaller than the total displacement observed in the **1** → **2** process and smaller than the shift expected according to the Spiesecke and Schneider correlation.[8] These results as well as other observations[21] indicate that when diamagnetic, aromatic species are obtained in reduction or oxidation processes, their total ^{13}C band displacements are in accord with the ^{13}C shift–charge density correlation.[8] In contrast, when nonaromatic and, in particular, antiaromatic systems result, this correlation is not observed.[21] The nonaromaticity of the acenaphthylene dianion (**5**) vs. the aromatic character of the aceheptylene dianion (**2**) is therefore emphasized. Another conspicuous difference between the ^{13}C patterns of **5** and **2** is concerned with the absorptions exhibited by the inner carbon (C_{11} and C_{13}, respectively). In the course of the reduction of **1** to **2** this band is paratropically shifted by 67.6 ppm, pointing toward a large negative charge on this carbon, whereas in the process **4** → **5** the inner carbon NMR band is diatropically shifted by 9.47 ppm. This indicates that no negative charge resides on the inner carbon atom of **5** as suggested by the second possibility of electrons distribution modes in the dianion (i.e., **5b**). Indeed, theoretical calculations[15] assign a very small negative charge density to C_{11} (Table IV). Thus, the NMR results as well as theoretical calculations point unequivocally toward a dianion in which the two "extra" electrons are delocalized in the periphery to afford a nonaromatic [^{11}C-13π] system, as depicted in **5a** (Scheme II). The clear similarity in mode of electrons distribution and in character between the dianion **5** and aceheptylene (**1**) should be considered in view of the fact that the two systems are isoelectronic.

Aceheptylene Dication (**3**). Perhaps the most interesting case is exhibited by the aceheptylene dication (**3**) being a 14-carbon and 12 π-electron system. Three different modes of distribution of these twelve π-electrons are possible (Scheme III): (**3a**) One positive charge located on the inner carbon atom C_{13} and the other spread over the 13 peripheral carbons. This distribution would result in a [13C-12π] peripheral conjugated system which, according to Platt's theory,[11] is expected to reveal antiaromatic character, slightly perturbed by the positively charged inner carbon. (**3b**) The two electrons are expelled in the course of the oxidation out of the periphery. Consequently, two positive charges delocalized only over the peripheral carbons are obtained and a nonaromatic [13C-11π] system results. (**3c**) The two positive charges obtained in the course of the oxidation process are spread over the two 7-membered rings, i.e., over the heptalene moiety. In this case aromatic character due to the aromaticity of heptalene dication would be established, upon which C_1–C_2 carbons act as an outer double bond perturbation.

NMR spectra and theoretical calculations[15] performed on **3** clearly suggest the third possibility of electrons distribution as the prevailing mode. The ^{1}H NMR chemical shifts (Table I; Figure 1) of the protons attached to the heptalene moiety are substantially low-field shifted in respect to the corresponding bands of the neutral system (center of gravity of 8.47 vs. 5.77 ppm). The observed total diatropic shift of the heptalene moiety protons is larger by ca. 1.5 ppm than the shift estimated by the charge density–^{1}H NMR shift correlation,[19] a shift caused only by the deshielding effect of positive charge density. The protons on the five-membered ring reveal a paratropic shift in the course of the 2-fold oxidation. This rather unexpected high-field shift is rationalized in terms of a decreased influence of the magnetic an-

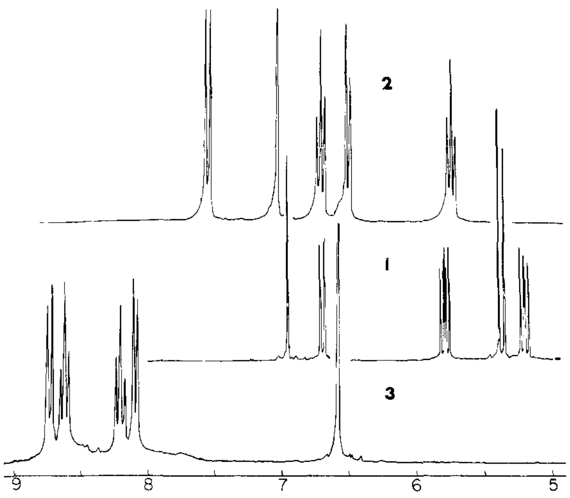


Figure 1. ^{1}H NMR spectra of aceheptylene (**1**), aceheptylene dianion (**2**), and aceheptylene dication (**3**).

isotropy sustained in the aromatic heptalene moiety on these protons. The decreased influence is due to the removal of C_1 and C_2 carbons from the heptalene skeleton, which is caused, in turn, by larger C_1–C_{11} and C_2–C_{12} bonds lengths. The ^{13}C NMR absorptions of **3** reveal the expected low-field displacements which amount to 371.66 ppm, in accord with the Spiesecke and Schneider correlation[8] and therefore in accord with the above discussion which relates the fulfillment of this correlation to the presence of diatropic, aromatic character. Theoretical calculations confirm our depiction of aceheptylene dication as a system composed of an aromatic heptalene moiety which is weakly coupled (and therefore perturbed) with an outer double bond, i.e., **3c**. Indeed, calculations assign a low degree of bond length alternation over the seven-membered rings and a very short bond length (1.3541 Å, characteristically vinylic) is assigned to the C_1–C_2 bond, while C_1–C_{11} and C_2–C_{12} bonds which attach the double bond to the heptalene moiety are estimated to be relatively long (1.4595 Å). The calculations assign a very small positive charge density to the C_1 and C_2 carbons (Table II) again, in accord with the third proposed electrons distribution. NMR spectra as well as $\omega\beta$ calculations clearly rule out the first and second distribution modes, i.e., **3a** and **3b** which lead to antiaromaticity and nonaromaticity, respectively.

An interesting point, concerning the aceheptylene dication (**2**) should be noted, i.e., the significant resemblance between this system and the acenaphthylene species (**4**). The two systems are aromatic, their aromaticity is due to the heptalene dication and naphthalene moieties being weakly perturbed by outer double bonds which are removed from the aromatic moiety by relatively long bonds. The resemblance, demonstrated by the mode of electrons distribution as well as by the σ-framework, is obviously attributed to the fact that the two systems are isoelectronic. On the basis of these observations it can be quite straightforwardly predicted that the hitherto unknown acepentylene dianion would be a stable compound endowed with aromatic character, with the two "extra" negative charges spread over the pentalene moiety.

Diprotonated Acenaphthoquinone (7). The oxidation of acenaphthylene results in an unstable radical cation. Nevertheless, we were able to draw information concerning the modes of electrons distribution over a 2-fold, positively charged acenaphthylene skeleton by studying the double protonation product (**7**) of acenaphthoquinone (**6**). Two positive charges which reside over the acenaphthylene skeleton enable, in principle, two different modes of electron distribution (Scheme IV): (**7a**) Two positive charges are delocalized over the peripheral carbons. In this case a [11C-9π] peripheral system is obtained, expected to reveal a nonaromatic character. (**7b**) One positive charge is located on the inner, central carbon atom C_{11}, while the other is spread over the entire periphery. This distribution mode would result in a [11C-10π] peripheral system, which, on the basis of Platt's model, should reveal an aromatic character.

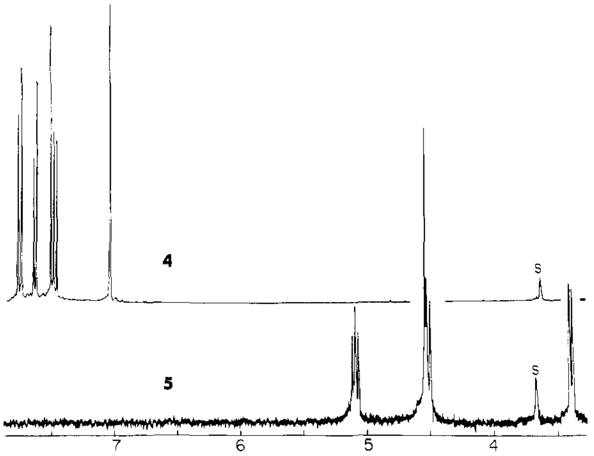
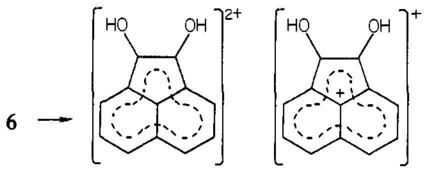


Figure 2. ^{1}H NMR spectra of acenaphthylene (**4**) and acenaphthylene dianion (**5**).

Scheme IV



The ^{1}H NMR patterns exhibited in the course of a diprotonation are more difficult to interpret in terms of aromaticity than the patterns revealed by a direct oxidation process. This is due to the conversion of the two keto into two hydroxyl groups caused by the diprotonation (Scheme IV), a conversion which results in a large alteration of the magnetic anisotropy associated with those groups. Even so, the low-field ^{1}H NMR band displacements due to the protonation point toward a large positive charge distribution over the naphthalene moiety. The total diatropic displacement indicates that the aromatic, diamagnetic character of **6** is not lost during the diprotonation process. The effects of the diprotonation are better studied by means of ^{13}C NMR spectroscopy (Table V). All the naphthalene-moiety carbons show diatropic shifts as a result of the protonation. Yet, the most striking downfield displacement is exhibiting by the inner carbon C_{11}, indicating a localized positive charge at this point. From the combined NMR data it seems that the diprotonated acenaphthoquinone is best depicted as an aromatic [11C-10π] system, in line with the second suggested mode of electron distribution, i.e., **7b**.

Electron Distributions, Chemical Stability, and σ-Framework: Correlation with Aromaticity and Antiaromaticity. Six neutral and negatively and positively charged systems were studied in terms of aromatic character and different modes of electron distributions, and these modes were examined in view of results obtained by theoretical calculations. Our observations point toward two general conclusions. The first conclusion may be stated as follows: a system would perform whatever can be performed with the purpose of gaining an aromatic character. If this goal is impossible to achieve, the system would "go all out" to avoid antiaromaticity and to sustain at least a nonaromatic character. This goal of approaching aromaticity is carried out via two interrelated mechanisms. The first consists of a distribution or redistribution of the π-electrons in such a mode that results in a conjugation path in which a Hückeloid ($4n + 2$) number of π-electrons are delocalized. In pericondensed systems such a mode can be achieved by two different structures: A ($4n + 2$) path of conjugation which consists only of the peripheral carbon atoms. The inner carbons atoms (neutral or bearing a positive or negative charge) act as a small perturbation to the peripheral conjugation. This situation is observed in the neutral, nonaromatic aceheptylene (**1**) being a ($4n + 1$; $n = 3$) peripheral system. It is exhibited as well by the aromatic aceheptylene dianion (**2**) with a Hückeloid

($4n + 2$; $n = 3$) number of π-electrons in the periphery which is coupled with a negatively charged inner carbon. The peripheral mode is revealed also by the acenaphthylene dianion, being a nonaromatic ($4n + 3$; $n = 2$) system which is its only mode of avoiding antiaromaticity, as well as by the aromatic diprotonated acenaphthoquinone (**7**) with ($4n + 2$; $n = 2$) peripheral π-electrons. In a sense, all those systems can be depicted as weakly perturbed annulenes. The second possible electron distribution mode is the establishment of a conjugation path over a part of the entire π system, those parts which do not participate in the conjugation act as an outer perturbation. This mode is exemplified by the aceheptylene dication (**3**) as well as by the neutral acenaphthylene (**4**). Both systems reveal an aromatic delocalization of 10 π-electrons over the heptalene and naphthalene moieties, respectively, their aromatic character slightly perturbed by an outer double bond.

The second mechanism by means of which a π system acquires aromaticity (or avoids antiaromaticity) is a modification of the σ-framework. When a carbon or a double bond acts as inner or outer perturbing agents, the system tends to reduce this perturbation by removing the source of perturbation as far as possible from the conjugation path. This is performed by making longer those bonds which connect the conjugation path with the perturbation source.

The relative simplicity of the described systems enables us to cross-examine some fundamental concepts concerning aromaticity, stability, charge distribution and the relationship between these factors. We mentioned above two different, representative criteria for aromaticity. Platt's peripheral model which assigns aromatic character to those polycyclic systems with $(4n+2)\pi$-electrons in the periphery. This structural criterion is based on purely theoretical considerations, i.e. HMO and free electron theory. The magnetic criterion relates aromaticity to ^{1}H NMR diatropic displacement – due to diamagnetic ring currents, and antiaromaticity with paratropicity caused by a paramagnetic contribution of low-lying excited states[24]. Our results clearly indicate that by allowing a minor modification to the Platt's approach, the two criteria—theoretical and experimental—coincide. When the character of a system is to be predicted, one should bear in mind that the periphery might be perturbed by an outer perturbing agent, such as a double bond, in the same sense that it can be perturbed by an inner factor. Thus, when applying Platt's peripheral criterion, the "effective" periphery, i.e., the path of conjugation which exhibits the largest contribution to the character of the system, should be considered. In view of our results this conjugation path is the one which will result in aromaticity or the one by which antiaromaticity will be avoided (e.g., the doubly charged heptalene moiety in **3**). The parallelism between the two different criteria for aromaticity is exhibited by neutral as well as by charged polycyclic systems—dianions and dications—and therefore seems to be a general feature. When aromaticity is predicted by the (modified) peripheral approach, a ^{1}H NMR diatropicity is always observed.

An interesting result is the unequivocal correlation between aromaticity and the sequel of the theoretical calculations.[15] If, in view of Platt's model, the acquirement of aromatic character calls for charge localization on an inner carbon (e.g., the aceheptylene dianion) or for electron delocalization over a part of the periphery (e.g., the aceheptylne dication), these requisites would be manifested by the calculations. Indeed, $\omega\beta$ estimates large negative charge density on C_{13} of **2**, to be contrasted with very small density in the peripheral dianion **5**. The calculations point toward a substantial positive charge delocalization over the heptalene moiety in **3** vs. a small charge distribution on the outer double bond (C_1 and C_2). Estimated bond lengths are also in accord with Platt's model and the magnetic criterion, revealing small alternation in the aromatic conjugation path and large values of those bonds which connect this path with perturbating centers. Systems expected and observed (by means of ^{1}H NMR) to be nonaromatic—such as **1**—are estimated to reveal substantial bond length alternation. The correlation between aromaticity and $\omega\beta$ calculations is of special and general interest. In principle, this semiempirical, HMO-based iterative method is virtually independent of any notion of aromaticity. The estimated charges and bond orders represent a wave function associated with the lowest content of energy. The correlation between aromaticity and stability (and between antiaromaticity and instability) is therefore demonstrated by means of the described tendency of conjugated systems to acquire aromatic character as well as by the correlation with theoretical calculations.

Conclusions

Neutral and charged pericondensed polycyclic systems exhibit a large general tendency to acquire aromatic character or, at least, to avoid antiaromaticity. This tendency is fulfilled by sustaining such modes of electron delocalization and charge distributions which would result in aromatic character or reduce antiaromatic contributions. On the basis of this observation, a $(4n + 2)$ π-electron path of conjugation offers the largest contribution to the total character of the system, and consequently, this path should be accounted for when applying Platt's approach. When this is done, Platt's theoretical model coincides with the magnetic, experimental criterion for aromaticity, the parallelism exhibited by neutral as well as charged systems. The charge distributions, as expected by the peripheral model and observed by NMR spectroscopy, are independently estimated by HMO-based calculation methods.

Experimental Section

Acenaphthylene was purchased from Aldrich Chemical Co. and recrystallized from EtOH. For the synthesis of aceheptylene, see ref 7.

The dianionic species have been prepared by reduction of the respective neutral compound with sodium. A wire of the metal was introduced to the upper part of an extended 5-mm NMR tube containing 10^{-2} M of the hydrocarbon dissolved in THF-d_8 (Aldrich). The frozen solution was degassed and then the tube was sealed under vacuum. The solution was brought into contact with the metal wire by turning the tube.

Aceheptylene dication was prepared by introducing the solid neutral hydrocarbon to a 5-mm NMR tube containing SbF_5–SO_2ClF, 1:1, solution which was kept at −40 °C and stirred vigorously. A sealed capillary containing acetone-d_6 was then introduced and the tube was sealed.

The diprotonation process of acenaphthoquinone was performed by adding a SbF_5–FSO_3H solution in SO_2 to a vigorously stirred SO_2ClF solution of the quinone kept at −40 °C, the acetone-d_6 capillary was introduced, and then the tube was sealed.

The NMR spectra were obtained on Bruker WH-300 pulsed FT spectrometer operating at 300.133 and 75.46 MHz for ^{1}H and ^{13}C, respectively. The field/frequency regulations were maintained by ^{2}H locking. The free induction decay signals were digitalized and accumulated on an Aspect-2000 computer (32K).

Registry No. **1**, 209-42-7; **2**, 85370-01-0; **3**, 85370-02-1; **4**, 208-96-8; **5**, 85389-79-3; **6**, 82-86-0; 7, 85370-00-9.

---

[24] Van Vleck, J. H. "Electric and Magnetic Susceptibilities"; Oxford University Press: Oxford, 1932; pp 262–276.