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The Charge Alternation Concept: Application to Cyclic Conjugated Doubly Charged Systems[†]

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Abstract: The application of the charge alternation concept to the charge distribution in doubly charged ions of mono- and polycyclic molecules (Figure 1) is described. The charge density in the systems under investigation was determined both by calculations and experiments (^{13}C NMR). The charges are not distributed uniformly over the entire system but appear in an alternating mode. This charge alternation—a basic characteristic of these systems—is a result of maximum donor–acceptor interactions which stabilize the systems. Rules are derived which enable the prediction of the charge distribution in the system without any need for elaborate calculations.

A host of spectroscopic data is available on doubly charged annulenes and polycyclic hydrocarbons as they were used as test cases for Hückel theory and as model compounds in the quest for understanding what "aromaticity" really means.[1-3] The changes in the aromatic nature of the systems upon charging was used to relate electronic structure with diatropicity or paratropicity.[3] The various modes of electron delocalization in polycyclic systems were discussed, and different approaches, such as the peripheral model of Platt[4] and Randič's conjugated circuits,[5] were proposed.

Recently, the concept of stabilization of charged systems by charge alternation was proposed.[6a] This concept explained satisfactorily the regioselectivity of polymetalation of allylic, benzylic, and propargylic systems. It was also extended recently to neutral systems, containing more than one donor or acceptor.[6b]

We feel therefore that a basic property of polycharged systems, namely their charge distribution, has been neglected. It will be demonstrated that the charges in polycharged systems are spread nonuniformly in such a way that certain positions act as acceptors of charge with their neighbors acting as donors. This mode of charge distribution results in maximum donor–acceptor interactions and hence in charge alternation. This charge alternation prevails regardless whether the charge distribution follows Platt's peripheral model[4] or Randič's conjugated circuit approach.[5]

It is in principle almost impossible to obtain fully cycloconjugated compounds with complete charge alternation, since most of these compounds have at least one axis or plane of symmetry traversing a bond in addition to the eventual plane of the ring. The existence of such elements of symmetry requires the molecule to have at least two neighboring atoms with the same charge. It is however possible that the molecule will polarize itself in such a manner that two or more subsystems will be formed, each of them revealing the phenomenon of charge alternation.

Examination of the calculated charge density and the experimental one as deduced from the carbon spectrum of charged polycyclic molecules (Figure 1) led us to formulate rules that can help us to divide the system and to predict how the charges will be placed in the compound. At first, one has to divide the system according to its element of symmetry bisecting one or more bonds thus forming two or more subsystems. These subsystems are then divided into starred and nonstarred sets,[7a] the starred set being the larger one. In general the main charge of the molecule will be distributed on the starred set in an alternating mode. In those cases where the starred set contains a relatively large number of quaternary carbons or involves severe Coulombic repulsions, the charge will be located on the nonstarred set of atoms. Severe Coulombic repulsions may occur when two or more highly charged starred atoms which belong to different subsystems, are adjacent.

Methodology

The dianions and dications presented in this study were chosen arbitrarily from the literature as well as from work done in our laboratory. The only criterion was the availability of their assigned carbon spectra. Representatives of several families of charged systems covering a wide range of K_c values ($\Delta\delta$ ^{13}C, ppm/e, vide infra)[7b] were included (Figure 1) to show the generality of our approach. As stated above, it is obvious that one cannot find a charge alternation in charged annulenes, such as the cyclooctatetraene dianion or dication, containing n carbons and having a C_n axis. For reasons of symmetry no such charge alternation can take place there. However, substituents might introduce a perturbation in those molecules which will lead to some charge alternation. In our analysis we included doubly charged systems of fused polybenzenoid and heterocyclic molecules (**1**–**7**), nonsymmetrical annulenes (**8**–**10**), and the acenaphthylene and its related compounds (**11**–**14**). We also included charged molecules containing $4n\pi$ conjugated circuits such as dianions of cyclooctatetraene derivatives (**15** and **16**) and the biphenylene (**17**) as well as the nonalternant dianions of dibenzo[*b*,*f*]pentalene (**18**), azulene (**19**), and *s*-indacene (**20**) (Figure 1).

The charge alternation concept was examined in these systems on two levels, computationally and experimentally. Therefore, each carbon atom in the charged systems is characterized by two numbers. One is the difference between the calculated charge density of this carbon in the neutral and in the respective doubly charged systems (Δq_π). The second number, an experimental value [$\Delta\delta^{13}$C] is the change of the ^{13}C chemical shift induced by the charging process of this very carbon atom. This change is taken as an experimental indication of the charge density and resides on this carbon.[7b-e] When the absorption band of the charged

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[†] A tribute to Professor E. J. Corey on the occasion of his 60th birthday.

(1) (a) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784. (b) Streitwieser, A.; Suzuki, S. *Tetrahedron* **1961**, *16*, 153. (c) Lawler, R. G.; Ristagno, C. V. *J. Am. Chem. Soc.* **1969**, *91*, 1534. (d) Oth, J. F. M.; Baumann, H.; Gilles, J.-M.; Schröder, G. *J. Am. Chem. Soc.* **1972**, *94*, 3498. (e) Paquette, L. A.; Photis, J. M.; Ewing, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 3538. (f) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937.

(2) For selected reviews, see: (a) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Fortsch. Chem. Forsch.* **1970/1971**, *16*, 103. (b) Young, R. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 261. (c) Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 296. (d) Müllen, K. *Chem. Rev.* **1984**, *84*, 603. (e) Müllen, K.; Huber, W. *Acc. Chem. Res.* **1986**, *19*, 300. (f) Rabinovitz, M., *Top. Curr. Chem.* **1988**, *146*, 101.

(3) (a) Mitchell, R. H.; Kopfenstein, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 4931. (b) McQuilkin, R. M.; Garratt, P. J.; Sondheimer, E. *J. Am. Chem. Soc.* **1970**, *92*, 6682. (c) Minsky, A.; Meyer, A. Y.; Poupko, R.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 2164. (d) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785. (e) Müllen, K.; Unterberg, H.; Huber, W.; Wennerström, O.; Norinder, U.; Tanner, D.; Thulin, B. *J. Am. Chem. Soc.* **1984**, *106*, 7514.

(4) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

(5) Randič, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.

(6) (a) Klein, J. *Tetrahedron* **1983**, *39*, 2733. (b) Klein, J. *Acc. Chem. Res.*, submitted for publication.

(7) (a) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975; p 74. (b) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (c) O'Brian, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (d) Olah, G. A.; Matescu, G. D. *J. Am. Chem. Soc.* **1972**, *92*, 1430.

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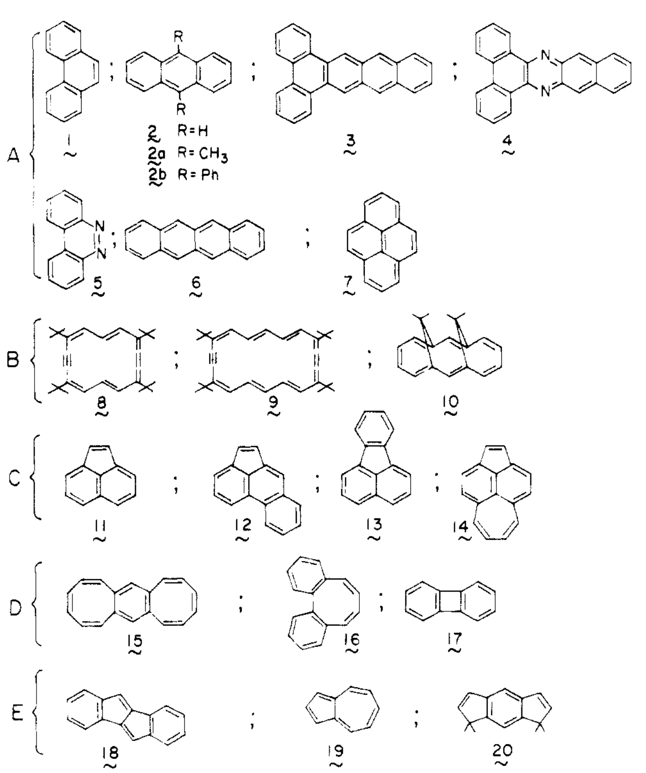

Figure 1. The parent molecules from which were derived the charged systems.

system is at higher field than that of the neutral system, the $\Delta\delta^{13}C$ value is positive regardless of whether the charged system is an anion or a cation. Although there are many more fully assigned proton spectra of charged systems than assigned carbon spectra, we decided to use carbon-13 data because of the strong dependence of the proton chemical shift on anisotropic effects. The two-electron reduction or oxidation processes generally result in a change or even inversion of the aromatic nature, namely the diatropicity or the paratropicity of the system under investigation are interchanged. These anisotropic effects have a large effect on the proton chemical shifts according to their location in the molecules.[8a] Therefore, the changes in the ^1H NMR chemical shift may be misleading as they are by no means governed by charge density effects only. Carbon-13 chemical shifts, however, are much less sensitive, in general, to anisotropic effects, and when no change in the hybridization of the carbon occurs, the major effect that contributes to the change in the chemical shift is the charge density.[8b] Although it has been shown recently that carbon chemical shifts are also sensitive to anisotropic effects, especially in paratropic polyanions,[7b] the change in the carbon chemical shift caused by the reduction process is still one of the best indirect measures for charge density. It has been shown that the sum of the changes in the carbon chemical shift per electron (K_c) for π-conjugated anions decreases as the paratropicity of the system increases.[7b] It will be shown that although the magnitude of K_c varies drastically, the charges always appear in an alternating mode.

There are reports in which there is no assignment of the carbon spectra of the neutral parent compound. In these cases the numbers that are reported are the ^{13}C chemical shifts of the carbon atoms of the charged system [$\delta^{13}C$] and the respective calculated charge density q_π. In some cases where it was difficult to assign the carbon spectra (especially quaternary carbon atoms), some authors used the calculated π-charge density and gave tentative assignments of the spectra, which led to circular argumentation. Therefore, we have chosen classical systems which were investigated by various groups and in which there is a general agreement on the assignment of the carbon spectra. For some recently prepared dianions, we used 2D-$^{13}C/^1H$ chemical shift correlation experiments[8c,d] which give an unambiguous assignment of the carbon spectra. Where the cited work does not give calculated charge densities, we completed the data by carrying out Hückel $\omega\beta$ calculations which were used and tested successfully in our laboratory.[9]

The Charge Alternation Concept

The charge alternation concept was introduced as a directing effect which explains the orientation of the polymetalation.[6] It was found that if there is a metalation of one of the starred atoms, the additional metalations will take place at other starred atoms. Geminal polymetalation was sometimes found to be preferred to the metalation at an unstarred position when there was no possibility of a successive metalation at other starred atoms of the system. It was also found that the central carbon in trimethylene-methane dianion bears a small positive charge.[10a] Moreover, it was pointed out by Gimarc that in some families of molecules "the charge densities are not all equal".[10b] In view of these results and other observations in the polymetalation of xylenes[10c] and acetophenones,[10d] it was concluded that if we divide a charged system into starred and nonstarred sets of atoms, the most stabilized structure is the one in which charge of the same sign is on the same set of atoms.[7a] This leads to a charge distribution in which there is a maximum number of donor-acceptor interactions. In electron-transfer reactions where the geometrical changes are minor, one would expect to get an uneven electron distribution when this is allowed by symmetry. The charge will be delocalized, and two adjacent atoms will usually have opposite signs of the charge. In such a way, one atom will act as an acceptor relative to its neighboring atoms. It must be emphasized that in dianions a negative charge may sometimes appear on nearly all the atoms, but then the magnitude of negative charge density will be alternating. This charge alternation seems to be of Coulombic origin rather than due to orbital interactions or to resonance. This effect must therefore be a very important one in ions and even more so in doubly charged systems; we assumed that it will be manifested even in fully conjugated or aromatic systems where näively one would expect nearly equal charge distribution in the entire molecule (vide infra).

Results and Discussion

The charge density distribution in polybenzenoid and heterocyclic charged systems (**1**–**7**, Figure 2) generally agrees with the charge alternation concept.

Phenanthrene dianion (**1**$^{2-}$),[11] which is a paratropic system with K_c equal to 52 ppm/e, is a good example for the applicability of the method, consisting of dividing the molecule into two odd carbon fragments. Bisecting **1**$^{2-}$ with the plane of symmetry across the C_9–C_{10} and C_{4a}–C_{4b} bonds gives two subsystems reminiscent of the benzylic fragments. In each of these fragments the charge alternation is like the one in the benzylic anion with relatively low charge density on C_{4a} and C_{4b} caused by Coulombic repulsion. Compare, for example, the differences in the chemical shift and the calculated charge density of the starred atoms $C_{9\ 10}$, $C_{1\cdot8}$, and $C_{3:6}$ with the nonstarred carbons $C_{2:7}$, $C_{4:5}$, and $C_{8a:10a}$ in the phenanthrene dianion (**1**$^{2-}$). It is interesting to note that for the nonstarred carbons $C_{2\cdot7}$ of **1**$^{2-}$ calculation predicts a small *positive* charge in contrast to the high negative charge of their starred neighbors ($C_{1:3}$ and $C_{6:8}$). This calculation is corroborated by the unusual down field shift (10.7 ppm) of the $C_{2:7}$ absorption band in the phenanthrene dianion (**1**$^{2-}$). From the two types of qua-

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(8) (a) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 81–84. (b) Günther, H. *NMR Spectroscopy*, Wiley: New York, 1980; p 367. (c) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. (d) Turner, D. L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1985**, *17*, 281.

(9) Modified $\omega\beta$ calculations on Coulomb integrals: (a) Berson, J. A.; Evleth, E. M., Jr.; Mannatt, S. L. *J. Am. Chem. Soc.* **1965**, *87*, 2801. (b) Boyd, G. V.; Singer, N. *Tetrahedron* **1966**, *22*, 3383. (c) Wohl, A. J. *Tetrahedron* **1968**, *24*, 6889.

(10) (a) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275. (b) Gimarc, B. M. *J. Am. Chem. Soc.* **1982**, *105*, 1979. (c) Klein, J.; Medlik-Balan, A. *J. Am. Chem. Soc.* **1977**, *99*, 1473. (d) Klein, J.; Medlik-Balan, A. *J. Org. Chem.* **1976**, *41*, 3307.

(11) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 1296.

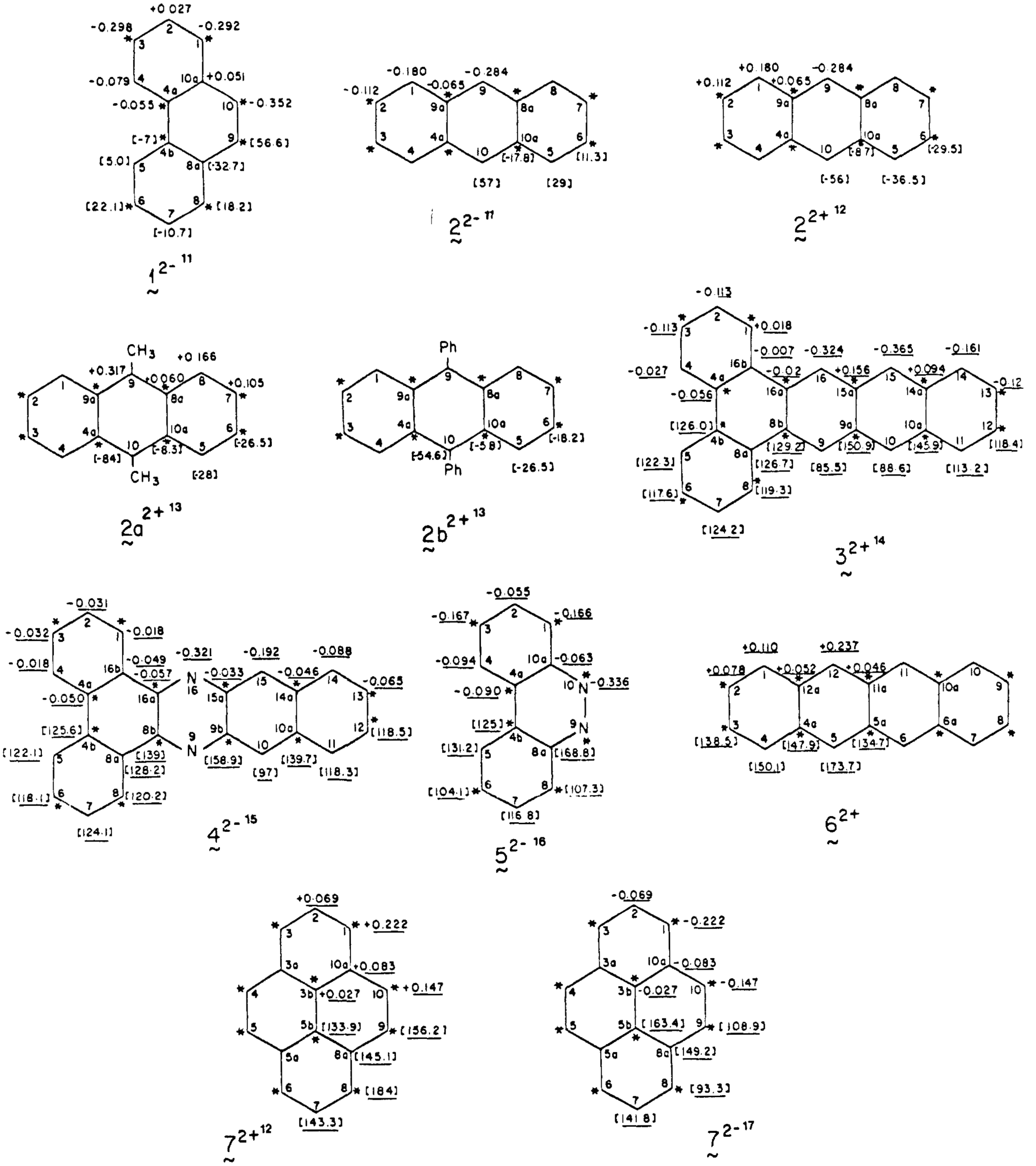

Figure 2. Calculated charge densities and ^{13}C NMR chemical shifts [$\Delta\delta^{13}$C or δ^{13}C] of carbocyclic and heterocyclic doubly charged systems (see text).

ternary carbons of the phenanthrene dianion ($\mathbf{1}^{2-}$) the nonstarred atoms $C_{10a;8a}$ are predicted to accommodate positive charge, a result which is in line with the extreme down field absorptions of their ^{13}C NMR band ($\Delta\delta^{13}C = -32.7$ ppm, Figure 2).

In the anthracene dianion ($\mathbf{2}^{2-}$)[11] bisection across the C_2–C_3, C_{4a}–C_{9a}; C_{8a}–C_{10a}, and C_6–C_7 bonds leads again to two odd-carbon fragments. However, the main portion of the charge is not located on the starred set because of the four adjacent carbons of similar charge in the two substructures which interact resulting in a pronounced Coulombic repulsion. The nonstarred set has also the advantage of not including quaternary carbons which accommodate negative charges with difficulty. Therefore, in this case the charges of $\mathbf{2}^{2-}$ are located on the nonstarred set of carbons and in distribution in an alternating mode.

A similar picture is revealed by the anthracene dication ($\mathbf{2}^{2+}$)[12] and its dimethyl and diphenyl derivatives ($\mathbf{2a}^{2+}$, $^{2}\mathbf{b}^{2+}$),[13] which have the positive charges located on the same atoms as the negative charge in the dianion ($\mathbf{2}^{2-}$, see Figure 2). In the case of $\mathbf{2a}^{2+}$ the differences in $\Delta\delta^{13}$C of the nonstarred positions $C_{1;4;5;8}$ compared with the starred position $C_{2;3;6;7}$ are very small (1.5 ppm). These small differences are expected since a very large amount of positive

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[12] The carbon spectra of $\mathbf{2}^{2+}$, $\mathbf{6}^{2+}$, and $\mathbf{7}^{2+}$ are taken from Forsyth and Olah (Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086). The data for **2** are taken from ref 11. The calculated charge densities were obtained from $\omega\beta$ calculations (see Experimental Section).

[13] Olah, G. A.; Singh, B. *J. Org. Chem.* **1983**, *48*, 4830. The calculated charge densities were obtained from $\omega\beta$ calculations (see Experimental Section).

charge of $\mathbf{2a}^{2+}$ is located at $C_{9:10}$ ($\Delta\delta^{13}C$ = 84 ppm). This explanation is in line with experimental data of the anthracene dication ($\mathbf{2}^{2+}$) and its diphenyl derivative ($\mathbf{2b}^{2+}$). In these two charged systems of the same topology, there is much less positive charge at position $C_{9:10}$ ($\Delta\delta^{13}C$ are ca. 55 ppm), and, consequently, the charge alternation is much more pronounced in the rest of the molecules.

The dibenzo[*a*,*c*]tetracene dianion ($\mathbf{3}^{2-}$)[14] and its heterocyclic analogue tribenzo[*a*,*c*,*i*]phenazine dianion ($\mathbf{4}^{2-}$)[15] are two complex systems that were prepared and investigated in our laboratory. Due to the complexity of the systems and their unusual charge distribution, we used 2D $^{13}C/^{1}H$ correlation spectroscopy[8b,c] in order to get an unambiguous assignment of the carbon spectra. In these two cases an interesting observation emerges. Most of the charge is located over the linear part of the molecules (the so called "anthracene"[14] and the "phenazine"[15] moieties, respectively, and the charge alternation concept explains well the calculated and the experimental results in these parts of the molecules. The calculation predicts that the quaternary carbons $C_{9a:15a}$, $C_{10a:14a}$ of the *negatively* charged part of dibenzo[*a*,*c*]tetracene dianion ($\mathbf{3}^{2-}$) accommodate relatively high *positive charges*. Positions $C_{9:16}$ and $C_{10:15}$ accommodate the highest negative charge density as depicted by calculation (-0.324 and -0.365 unit of charge) and their chemical shifts (85.5 ppm and 88.6, respectively). Therefore, these two highly negatively charged atoms induce a high *positive* charge (+0.156) on the atom between them to afford a real donor-acceptor interaction. Indeed C_{9a} and C_{15a}, the starred carbons between these two unstarred carbons ($C_{9:10}$ and $C_{15:16}$), absorb at 150.9 ppm which is the lowest absorption band found in the ^{13}C spectrum of $\mathbf{3}^{2-}$ (Figure 2). It should be noted that the carbon chemical shifts of **3** are in the range of 132.8-122.7 ppm. Even more so, the additional carbons which are predicted by calculation to have a *positive charge* are the starred C_{10a} and C_{14a} atoms which again are between two unstarred and highly negatively charged carbons $C_{10:11}$ and $C_{14:15}$, respectively.

In the benzo[*c*]cinnoline dianion ($\mathbf{5}^{2-}$)[16] and the tetracene dication ($\mathbf{6}^{2+}$)[12] the charge alternation operates well in the entire system. The benzo[*c*]cinnoline dianion ($\mathbf{5}^{2-}$) which is the heterocyclic analogue of phenanthrene dianion ($\mathbf{1}^{2-}$) has a charge distribution similar to that of $\mathbf{1}^{2-}$. The same division can be made into fragments with the nitrogen atoms placed in positions that accommodate much negative charge. Tetracene dication $\mathbf{6}^{2+}$ behaves like $\mathbf{2}^{2+}$ and for the same reason, i.e., a Coulombic repulsion between the starred atoms of the two subsystems, causes the location of the charges on the unstarred sets, which in addition does not include quaternary carbon atoms.

For the pyrene molecule **7** the results of the dication $\mathbf{7}^{2+}$[12] and the dianion $\mathbf{7}^{2-}$ resemble one another (Figure 2), and we chose to concentrate on the dianion which has recently been reexamined.[17] The pyrene dianion was found to be paratropic, and, accordingly, its K_c values are rather low (20 and 5 ppm/e for the dilithium and disodium salts, respectively). Nevertheless, its charge distribution generally agrees with the charge alternation concept as concluded both from calculation and from the carbon chemical shifts of $\mathbf{7}^{2-}$ (Figure 2). Compare, for example, the charge density and the ^{13}C NMR bands of the C_2 and C_7 which are nonstarred carbon atoms (-0.069 and 141.8 ppm, respectively) with their two starred neighbors $C_{1:3}$ and $C_{6:8}$ (-0.222 and 93.3 ppm, respectively). The quaternary nonstarred neighbors of $C_{1:3:6:8}$ accommodate only -0.083 units of charge and absorb at low field (149.2 ppm), while the starred atoms $C_{4:5:8:10}$ accommodate more charge, i.e., -0.147 units of charge (Figure 2), and their chemical shift is at relatively high field (108.9 ppm). The only exception in $\mathbf{7}^{2-}$ as well as in $\mathbf{7}^{2+}$ appears at the central carbons C_{3b} and C_{5b}. These positions are starred positions and are expected to accommodate high charge density. It must be emphasized that not only their chemical shift deviates but also the calculated charge density. The fact that also the calculated charge densities of C_{3b} and C_{5b} deviate demonstrates that the origin to these deviations are not the results of anisotropic effects only, so one has to search for real electronic factors affecting these deviations. Calculation predicts that the HOMO of pyrene dianion ($\mathbf{7}^{2-}$) has a node through carbons $C_{2:3b:5b:7}$ which serves as an indication of the fact that no real net charge is to be expected on these carbon atoms although these carbons are part of the starred subsystem. One plausible explanation for the deviation of C_{3b} and C_{5b} may be that those atoms are surrounded by atoms with high electron density, and, therefore, the location of negative charge in them is not favorable energetically. This presents a different kind of charge alternation, a through-space rather than a through bond phenomenon.

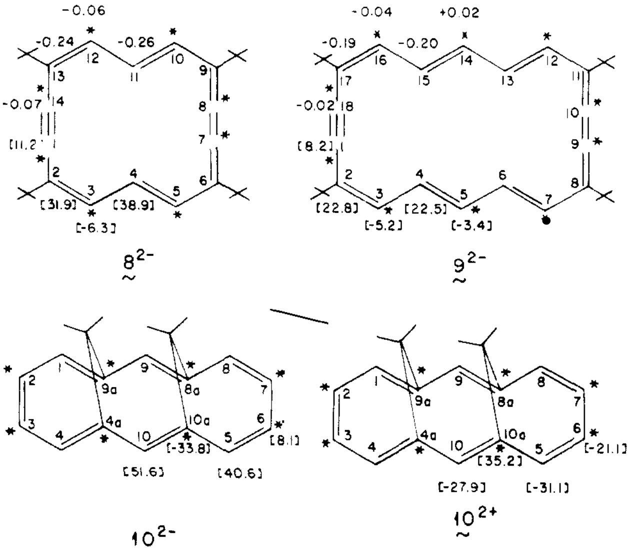

Figure 3. Calculated charge densities and ^{13}C NMR chemical shifts [$\Delta\delta^{13}C$ or $\delta^{13}C$] of charged annulenes (see text).

An important family of charged systems is shown in Figure 3. These charged systems of monocyclic annulenes (**8**-**10**) behave exactly as predicted by the charge alternation concept. Dianion $\mathbf{8}^{2-}$[18] can be divided by a plane of symmetry bisecting C_1-C_{14} and C_7-C_8 bonds into two odd carbon fragments. The charge in these dianions is distributed on the unstarred set of carbons in an alternating mode as in the case of anthracene dianion ($\mathbf{2}^{2-}$) or dication ($\mathbf{2}^{2+}$) and tetracene dication ($\mathbf{6}^{2+}$) and for the same reasons. It should be noted that in the systems $\mathbf{8}^{2-}$,[18] $\mathbf{9}^{2-}$,[18] $\mathbf{10}^{2-}$,[2d] and $\mathbf{10}^{2+}$[2d] there is no deviation at any of their many carbons from the charge alternation predictions. It can be seen that when there is no other important factor the charge alternation governs nearly completely the charge distribution in the charged system.

In the third group of structurally related charged systems, the charge alternation concept works nicely although these compounds have more complicated structures (Figure 4). The charge in $\mathbf{11}^{2-}$ is distributed over the entire periphery, which is in line with a previous report that acenaphthylene dianion ($\mathbf{11}^{2-}$)[19,20] can be regarded as an annulene with a [13πe;11C] periphery.[19,21a] However, the calculated charge density and the experimental

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[14] Carbon spectra are taken from the following: Frankel, Y.; Cohen, Y.; Rabinovitz, M., to be published. Calculated charge densities are taken from the following: Minsky, A.; Rabinovitz, M. *J. Am. Chem. Soc.* **1984**, *106*, 5755.

[15] Only the protonated carbons of $\mathbf{4}^{2-}$ were assigned by 2D NMR correlation C/H spectroscopy (this work); the calculated charge densities appear in the following: Cohen, Y.; Meyer, A. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1986**, *108*, 7039.

[16] Assignment was carried out by 2D NMR correlation spectroscopy (this work), and the calculated charge densities appear in the following: Minsky, A.; Cohen, Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1985**, *107*, 1501.

[17] Experimental data taken from the following: Eliasson, B.; Lejon, T.; Edlund, U. *J. Chem. Soc., Chem. Commun.* **1984**, 591. The calculated charge densities were obtained from ωβ calculations (see Experimental Section).

[18] Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403.

[19] Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975.

[20] Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1837.

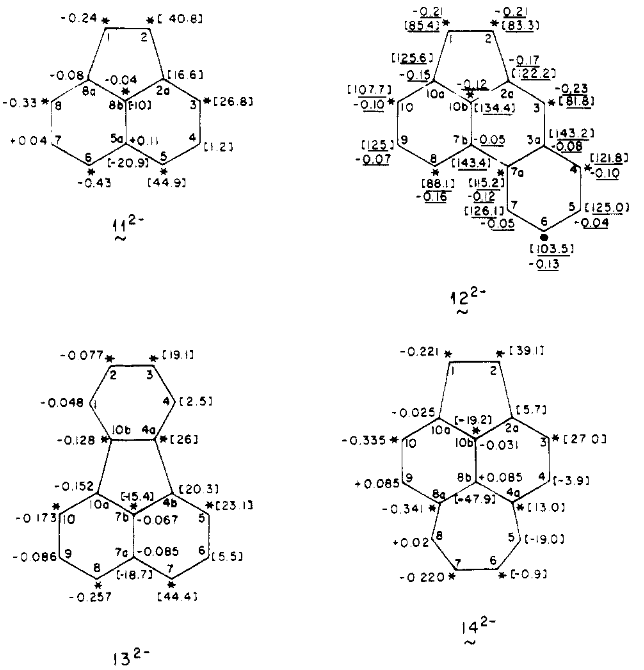

Figure 4. Calculated charge densities and ^{13}C NMR chemical shifts [$\Delta\delta^{13}C$ or $\delta^{13}C$] of acenaphthylene dianion (11^{2-}) and related systems (see text).

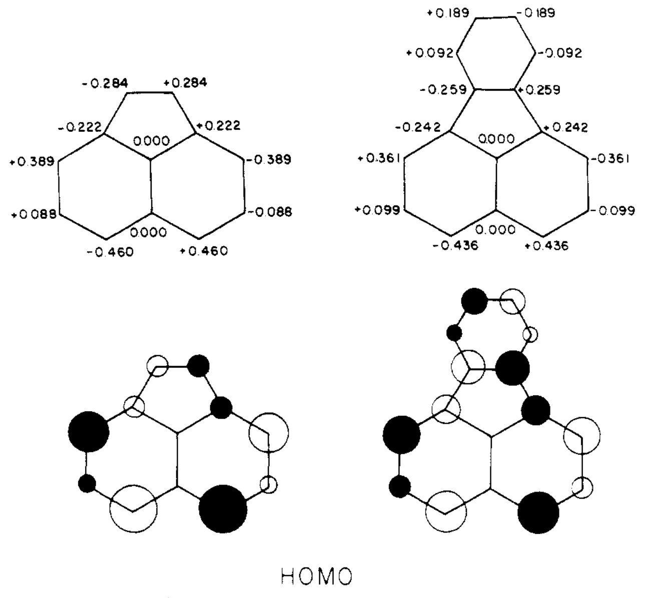

Figure 5. The coefficients of the HOMO's of the acenaphthylene dianion (11^{2-}) and fluoranthene dianion (13^{2-}), as obtained by $\omega\beta$ calculations.

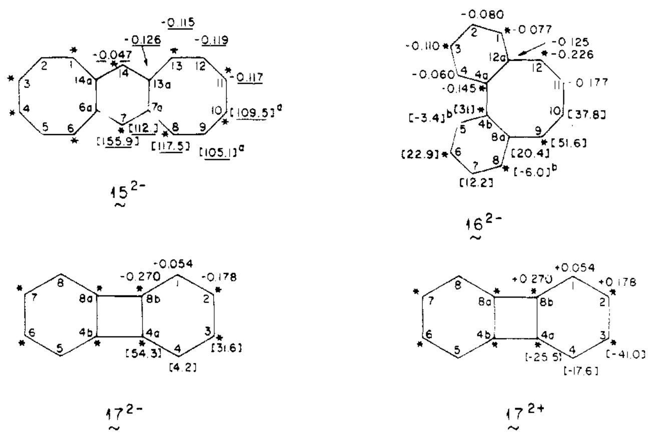

Figure 6. Calculated charge densities and ^{13}C NMR chemical shifts [$\Delta\delta^{13}C$ or $\delta^{13}C$] of system containing $4n\pi$ conjugated circuits (see text).

differences of the carbon chemical shift [$\Delta\delta^{13}C$] follow the charge alternation predictions. Despite the fact that the five-membered rings tend to attract the charges to its carbon atoms it appears that much of the charge resides on the starred carbons $C_{5:6}$ and $C_{3:8}$. The charge density on carbons C_1 and C_2 of 11^{2-} is therefore lower than expected after bisection of the molecule across the C_{1-2} bond and along the C_{5a-8b} bond. Most of the charge is at positions C_5 and C_6 rather than at C_3 and C_8. At the nonstarred carbons C_4 and C_7 calculations predict a small positive charge which is totally in line with the low high field shift ($\Delta\delta^{13}C$ = 1.2 ppm) observed for these carbons. It should be noted that these charge distributions explain the selective protonation of 11^{2-} at $C_{5:6}$ in a mixture of THF/NH_3.[21b]

In the case of acephenanthrylene dianion (12^{2-}) we assigned the carbon spectrum of the protonated carbons by means of a 2D $^{13}C/^{1}H$ correlation experiment. The additional ring has only a minor effect on the charge distribution,[21a] and charge alternation generally prevails in the acephenanthrylene dianion (12^{2-}) as well as in fluoranthene dianion (13^{2-})[22] (see Figure 4). In 11^{2-} and 13^{2-} there is one disagreement between the experimental and calculated charge density with the prediction based on the charge alternation concept, notably the charge of the central quaternary carbons. These carbons are part of the starred set of carbons (Figure 4) and therefore are expected to accommodate a relatively high charge density which they do not. The deviation of the central quaternary carbons of 11^{2-} and 13^{2-} is manifested by the HOMO's of these dianions which have a node bisecting the five-membered ring along these central atoms (resulting in an annulenic type path of electron delocalization) (Figure 5). Here again a different mechanism, namely the through spece charge alternation mechanism, may be operative as suggested for the central bond of the pyrene dianion (7^{2-}).

In the isopyrene dianion (14^{2-})[22] in which the carbon center of gravity is down field to that of **14** (K_c = −1 ppm), the charge is distributed in an alternating mode as can be seen by comparing the data for the starred carbons $C_{1,2}$, $C_{3:10}$, and $C_{4a,8a}$ with the nonstarred carbon $C_{2a:10a}$, $C_{4:9}$, and $C_{5:8}$. It seems that calculation overestimates the charge density in the seven-membered ring as can be concluded by comparing the computed charge density for $C_{6:7}$ (−0.220) with the experimental shift of their ^{13}C NMR absorption band ($\Delta\delta^{13}C$ = 0.9 ppm). It is interesting to note that the ^{13}C NMR absorption band of the starred quaternary carbon (C_{10b}) which is expected to act as an acceptor of negative charge in 14^{2-} is shifted to *low field* by 19.2 ppm, and calculation predicts only a small negative charge (−0.031) for this position. At first sight these results seem to deviate from our predictions; however, comparison of these data with those of its nonstarred neighbor atom (C_{8b}) is instructive. The ^{13}C NMR band attributed to this carbon is shifted downfield by not less than *47.9* ppm and calculation predicts a relatively *high positive* charge density for it (+0.085 units of charge).

The next family of compounds consists of molecules containing a four- or eight-membered ring as part of them (Figure 6). We chose to concentrate on the charged biphenylenes (17^{2-} and 17^{2+})[24] that were investigated recently by modern NMR techniques which enable an unambiguous assignment of their simple carbon spectra. The biphenylene dianion (17^{2-}) was shown to be diatropic with a very high proportionality constant (K_c) of 174 ppm per electron.[24]

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[21] (a) Only protonated carbons were assigned by 2D $^{13}C/^{1}H$ correlation spectroscopy. Data were taken from the following: Cohen, Y.; Roelofs, N. H.; Reinhardt, G.; Scott, L. T.; Rabinovitz, M. *J. Org. Chem.* **1987**, *52*, 4207. (b) Müllen, K.; Huber, W.; Neumann, G.; Schneiders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801.

[22] Experimental data were taken from the following: Becker, B. Ch.; Huber, W.; Schneiders, C.; Mullen, K. *Chem. Ber.* **1983**, *116*, 1573. Calculated charge densities given for 13^{2-} were obtained from $\omega\beta$ calculations (this work).

[23] Experimental data were taken from the following: Paquette, L. A.; Ewing, G. D.; Traynor, S.; Gardlik, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 6115. Calculated charge densities were obtained by $\omega\beta$ calculations (this work).

[24] Benken, R.; Finneiser, K.; von Puttkamer, H.; Günther, H.; Eliasson, B.; Edlund, U. *Helv. Chim. Acta* **1986**, *69*, 955.

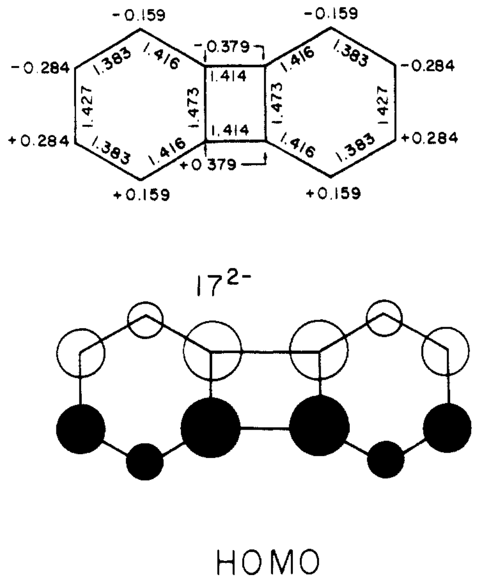

Figure 7. The coefficients of the HOMO and bond length of the biphenylene dianion (17^{2-}) as obtained by $\omega\beta$ calculation.

Most of the charge is concentrated, as expected, in the central cyclobutadiene and is by symmetry of the molecule equally distributed on the four carbons. The high charge density in the four-membered ring induces on the attached phenyls charge alternation. It is interesting to note that calculation predicts that upon the two-electron reduction of biphenylene (**17**) there is a dramatic structural change. The C_{4a}–C_{8b} and C_{4b}–C_{8a} bonds became very long (1.472 Å) thus rendering the biphenylene dianion **17**$^{2-}$ reminiscent of a [12]annulene dianion. The calculated bond lengths of the biphenylene dianion **17**$^{2-}$ and the coefficients of its HOMO are shown in Figure 7. The same holds for the biphenylene dication (**17**$^{2+}$).

The charged systems derived from **18–20** which are shown in Figure 8 have more than one odd-membered ring. It is interesting to note that the calculated charge density of **18**$^{2-}$ as well as the experimental data show the expected charge alternation except at $C_{1:6}$ and $C_{2:7}$.[25] Although the calculation gave higher charge density at the starred atoms $C_{1:6}$, the differences in the carbon chemical shift $\Delta\delta^{13}C$ is larger for $C_{2:7}$ (12 ppm compared with 6.0 ppm for $C_{1:6}$). As the assignment was carried out by selective decoupling experiments, there is no reason to assume an incorrect assignment. The other pairs of carbons of **18**$^{2-}$ that do not behave as expected according to the charge alternation concept are the quaternary carbons $C_{4a:9a}$ and $C_{4b:9b}$ in which only the calculated charge density is in line with our predictions. This, however, may indicate an incorrect assignment of the quaternary carbons, which were assigned tentatively.

The azulene dianion (**19**$^{2-}$) was reexamined recently.[26] A close inspection of the data reveals that there is a charge alternation in the five-membered ring but it seems that the azulene dianion (**19**$^{2-}$) behaves as if it were composed of two substructures—a five-membered ring anion linked to a pentadienylic anion. In order to get more insight into this system, we carried out calculations to obtain information on the bond length of the azulene (**19**) and its dianion (**19**$^{2-}$) (Figure 9). It was found that the bonds which connect the five-membered ring with the pentadienylic fragment become very long on going from neutral **19** (1.405 Å) to **19**$^{2-}$ (1.475 Å). There is considerable charge alternation in each of the two fragments of the azulene dianion (**19**$^{2-}$) (Figure 9). For example, the starred carbon C_6 is shifted by 69 ppm to high field; and its calculated charge density is −0.44 units of charge. Its nonstarred neighbors C_5 and C_7 have a positive charge +0.04 units each and are shifted to *downfield* by 11.1 ppm. The next pair of starred carbons C_8 and C_4 are shifted to high field by 37.2 ppm which is in line with the high negative charge found in calculation (−0.42 units of charge). On the basis of these observations and the calculated bond lengths we come to the conclusion that the best representation for azulene dianion (**19**$^{2-}$) is structure **21** (Figure 9). In this structure the system is split into two substructures namely a cyclopentadienyl anion and an acyclic pentadienyl anion connected by two "virtually single bonds". In each substructure the charge alternation prevails in a very pronounced way.

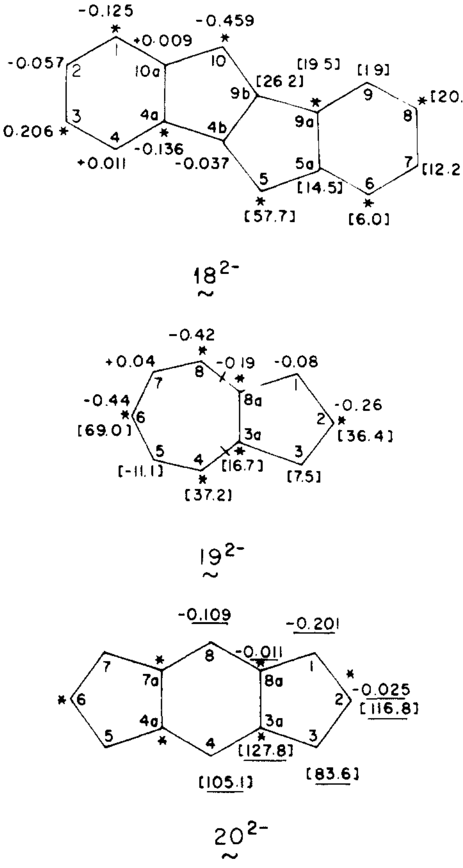

Figure 8. Calculated charge densities and ^{13}C NMR chemical shifts [$\Delta\delta^{13}C$ or $\delta^{13}C$] on nonalternant systems (see text).

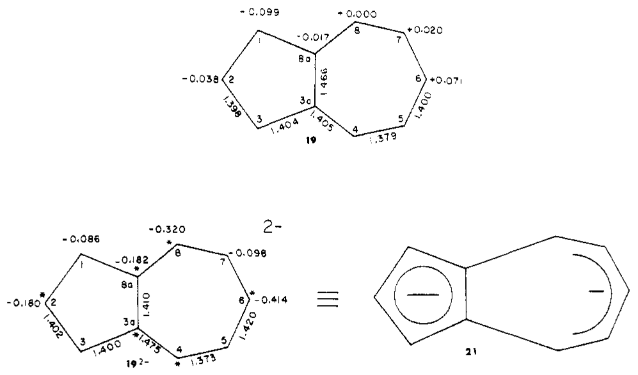

Figure 9. Calculated bond length of the azulene (**19**) and its respective dianion (**19**$^{2-}$) as obtained by $\omega\beta$ calculations.

The *s*-indacene dianion (**20**$^{2-}$)[28] which was prepared by double deprotonation with BuLi shows charge alternation, and in this case there is no exception either in the calculated charge density nor in the ^{13}C chemical shift. The agreement between the calculated charge densities with the ^{13}C chemical shifts of the nonstarred carbon $C_{1:3}$, $C_{4:8}$, and $C_{5:7}$ relative to the starred carbons

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(25) Eliasson, B.; Edlund, U. *Org. Magn. Reson.* **1983**, *21*, 322.

(26) Edlund, U.; Eliasson, B. *J. Chem. Soc., Chem. Commun.* **1982**, 950.

(27) Edlund, U.; Eliasson, B.; Kowalewski, J.; Trogen, L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1260.

(28) Katz, T. J.; Balogh, V.; Schulman, J. *J. Am. Chem. Soc.* **1968**, *90*, 734.

$C_{2:6}$, $C_{3a:4a:7a:8a}$ is obvious (Figure 8).

Conclusions

The charge alternation concept is presented, and its application to cyclic doubly charged conjugated systems is discussed. The charge density was deduced from calculation and compared with experimental data ($\Delta\delta^{13}C$ in the carbon NMR spectra). It can be concluded that charge alternation is indeed a characteristic feature of this type of compounds. It seems that in order to reduce Coulombic repulsions, the charge is not spread uniformly but is concentrated at certain positions in *an alternating mode*. This alternation leads to a donor–acceptor type interaction which is more stabilizing than a simple uniform charge distribution. Interestingly, it has been found that the more the negative charge is located on two carbons, the more is the *positive* charge concentrated on the atom in between them. We have presented rules which permit the prediction of the location of the main charges either on the starred or on the nonstarred set of subsystems. In the case of the charged annulenes there is no exception to the charge alternation rules, while in polycyclic systems the deviations, if any, are found particularly in the inner carbons of pericondensed systems.

In our study we describe examples in which the charge alternation prevails covering a wide range of K_c values from −1 ppm/e for $\mathbf{14}^{2-}$ up to the biphenylene case (**17**) for which K_c is equal to 174 ppm/e.[7b] Therefore, it can be concluded that the charge alternation which is a basic characteristic of these systems prevails regardless of the magnitude of K_c.

The approach presented here is very simple and empirical and seemingly rather näive. The charges in a dianion of an alternant hydrocarbon depend mainly on the HOMO of this dianion, and thus such a simple treatment as the one presented here cannot always be correct. However, one has to consider to what extent the HOMO of the dianion depends on the eventual distribution of the charges in the dianion, since it is the charge alternation stabilization that is the physical effect, and the MO's are only a manifestation of these effects. The fact that charge alternation does take place in diatropic and paratropic π-conjugated charged systems and that the charges there are distributed nonuniformly proves that this is a powerful and fundamental effect in chemistry.

Experimental Section

The procedure for the metal reduction process was as described previously.[3c,d,15,16] The 2D NMR spectra were obtained on a Bruker SY-200 pulsed FT spectrometer equipped with a pulse programmer operating at 200.133 and 50.32 MHz for ^1H and ^{13}C NMR, respectively. Field frequency regulations were maintained by ^2H locking. The free induction decay (FID) signals were digitized and accumulated on an Aspect-2000 computer. All 2D NMR experiments (such as COSY, NOESY, and $^{13}C/^1H$ correlation spectroscopy) used for assignment of spectra were carried out according to standard pulse sequences appearing in the Bruker Library (DISN 85). The MO calculations were performed by the "$\omega\beta$" technique[9] amplified by the habitual parameters. For =N- and the aromatic C–N and N–N bonds we used the following parameters:[9c] $\alpha(N) = \alpha(C) + 0.4\beta(C{-}C)$, $\beta(C{-}N) = \beta({-}C{-}C)$, $\beta(N{-}N) = \beta(C{-}C)$. For $\mathbf{2a}^{2+}$ the parameters were $\alpha(C_{9:10}) = \alpha(C) - 0.1\beta(C{-}C)$ and for the CH_3 substituents $\alpha(C) = \alpha(C) - 0.2\beta(C{-}C)$, $\alpha(\equiv H_3) = \alpha(C) - 0.5\beta(C{-}C)$, $\beta(C_{9:10}{-}C) = 0.7\beta(C{-}C)$, and $\beta(C{\equiv}H_3) = 2.5\beta(C{-}C)$. For $\mathbf{2b}^{2+}$ the $\beta(C{-}C)$ for the bond connecting the phenyl substituents was taken as $0.5\beta(C{-}C)$.

Registry No. 1, 85-01-8; $\mathbf{1}^{2-}$, 113584-95-5; **2**, 120-12-7; $\mathbf{2}^{2-}$, 113584-96-6; $\mathbf{2}^{2+}$, 34531-06-1; **2a**, 781-43-1; $\mathbf{2a}^{2+}$, 38418-02-9; **2b**, 1499-10-1; $\mathbf{2b}^{2+}$, 70470-09-6; **3**, 216-00-2; $\mathbf{3}^{2+}$, 113685-58-8; **4**, 216-01-3; $\mathbf{4}^{2-}$, 113584-97-7; **5**, 230-17-1; $\mathbf{5}^{2-}$, 94370-25-9; **6**, 92-24-0; $\mathbf{6}^{2+}$, 38418-05-2; **7**, 129-00-0; $\mathbf{7}^{2-}$, 95596-53-5; $\mathbf{7}^{2+}$, 60670-21-5; **8**, 113597-87-8; $\mathbf{8}^{2-}$, 113597-89-0; **9**, 113597-88-9; $\mathbf{9}^{2-}$, 113597-90-3; **10**, 14458-51-6; $\mathbf{10}^{2-}$, 113685-61-3; $\mathbf{10}^{2+}$, 113685-60-2; **11**, 208-96-8; $\mathbf{11}^{2-}$, 113584-98-8; **12**, 201-06-9; $\mathbf{12}^{2-}$, 113584-99-9; **13**, 206-44-0; $\mathbf{13}^{2-}$, 113685-59-9; **14**, 194-32-1; $\mathbf{14}^{2-}$, 69743-13-1; **15**, 10474-65-4; $\mathbf{15}^{2-}$, 113585-00-5; **16**, 217-22-1; $\mathbf{16}^{2-}$, 66560-56-3; **17**, 259-79-0; $\mathbf{17}^{2-}$, 72843-96-0; $\mathbf{17}^{2+}$, 62157-22-6; **18**, 248-58-8; $\mathbf{18}^{2-}$, 65583-99-5; **19**, 275-51-4; $\mathbf{19}^{2-}$, 78851-03-3; **20**, 70600-15-6; $\mathbf{20}^{2-}$, 113585-01-6.

Electrophilic Additions to 3-*C*-[(Methoxycarbonyl)methyl]-3-deoxy-D-ribofuranose Enolates: A Case of Unusually Efficient Non-Chelate-Enforced Chirality Transfer[†]

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Abstract: The enolates **4a,b** obtained from ester **3a** on deprotonation with lithium diisopropylamide in THF and THF/HMPA, respectively, add alkyl halides and benzaldehyde with >99% diastereoselectivity to form **3c–f**. The structure of **3b** was established by X-ray crystallography via the corresponding 5,6-diol **3i**. This unusually high chirality transfer is not due to a chelate-controlled mechanism, as the partially deoxygenated derivatives **9d**, **10d**, and **11c** show the same or a slightly diminished selectivity on deprotonation/methylation. The steric course of the enolate alkylation may be described as a "frontside" attack of the electrophile on reactive conformation A. Furthermore, the stereochemistry of the deprotonation of **3a,b** was investigated by using the stereospecifically deuteriated model compounds **21a–d** and **22**. It was shown that the amide base attacks from the "front side" of the molecule, the reactive conformation of the substrate now being of type B, in contrast to the alkylation.

Chirality may be incorporated into ester enolates by means of the alcohol (O-chiral case) or the carboxylic acid (C-chiral case) component. In either case, efficient stereocontrol of electrophilic additions to a prochiral enolate carbon may be exerted by chelate-enforced chirality transfer, particularly in chelate rings of sizes 5–7.[1] In contrast to the configurationally unrestricted O-chiral case, chelate formation in C-chiral ester enolates requires *E* geometry around the double bond. This demand contradicts Ireland's rule,[2] according to which *Z*-enolates are generated with

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[†] Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

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(1) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3B, p 1–110.

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