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

Yoram Cohen, Joseph Klein,* and Mordecai Rabinovitz*

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. Received August 17, 1987

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 (13C 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 under charging was used to relate electronic structure with diatropicity or paratropicity.4 The various modes of electron delocalization in polycyclic systems were related electronic structure with diatropicity or paratropicity. The demonstrated that the charges in polycharged systems are spread benzylic, and propargylic systems. It was also extended recently peripheral model4 or Randić’s conjugated circuit approach.5

Recently, the concept of stabilization of charged systems by charge alternation was proposed.6 This concept explained satisfactorily the regioselectivity of polynuclear systems aromatic. It was also extended recently to neutral systems, containing more than one donor or acceptor.6a

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 model4 or Randić’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 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.

A tributary to Professor E. J. Corey on the occasion of his 60th birthday.
Cyclic Conjugated Doubly Charged Systems

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

- **The Charge Alternation Concept**

The charge alternation concept was introduced as a directing effect which explains the orientation of the polymetallation. 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 polymetallation 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. Moreover, it was pointed out by Gimarc that in some families of molecules "the charge densities are not all equal". In view of these results and other observations in the polymetalation of xylene and acetoephone, 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. 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 systems. 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 so in doubly charged systems; we assumed that it will be manifested even in fully conjugated or aromatic systems where naively 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⁻⁻), which is a paratropic system with \( K_e \) 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 2D with the plane of symmetry across the \( C_7C_8 \) and \( C_4C_5 \) 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 \( C_6 \) and \( C_9 \) caused by Coulombic repulsion. Compare, for example, the differences in the chemical shift and the calculated charge density of the starred atoms \( C_7, C_8 \) and \( C_4, C_5 \) with the nonstarred carbons \( C_{12}, C_{13} \) in the phenanthrene dianion (1⁻⁻). It is interesting to note that for the nonstarred carbons \( C_{12} \) of \( 1⁻⁻ \) calculation predicts a small positive charge in contrast to the high negative charge of their starred neighbors \( (C_7, C_8) \). This is consistent with the usual down field shift (10.7 ppm) of the \( C_{12} \) absorption band in the phenanthrene dianion (1⁻⁻). From the two types of qua-

ternary carbons of the phenanthrene dianion (12-) the nonstarred atoms C12,6,12 are predicted to accommodate positive charge, a result which is in line with the extreme down field absorptions of their $^{13}$C NMR band ($\Delta^{13}$C = -32.7 ppm, Figure 2).

In the anthracene dianion (22-)12 bisection across the C2-C3, C5-C6, C8-C9, and C11-C12 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 22- are located on the nonstarred set of carbons and in distribution in an alternating mode.

A similar picture is revealed by the anthracene dication (22+)12 and its dimethyl and diphenyl derivatives (22+; 22+),13 which have the positive charges located on the same atoms as the negative charge in the dianion (22-, see Figure 2). In the case of 22+ the differences in $\Delta^{13}$C of the nonstarred positions C12,6,12 compared with the starred position C2,3 are very small (1.5 ppm). These small differences are expected since a very large amount of positive charge is concentrated on the nonstarred set of carbons.

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

[12] The carbon spectra of $2e^+$, $6e^+$, and $7e^+$ 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 ab initio calculations (see Experimental Section).

[13] Olah, G. A.; Singh, B. J. Org. Chem. 1983, 48, 4830. The calculated charge densities were obtained from ab initio calculations (see Experimental Section).
charge of $2a^+$ is located at $C_{210}$ ($\Delta^{12}C = 84$ ppm). This explanation is in line with experimental data of the anthracene dication ($2^+$) and its diphenyl derivative ($2b^+$). In these two charged systems of the same topology, there is much less positive charge at position $C_{210}$ ($\Delta^{12}C$ are ca. 55 ppm), and, consequently, the charge alternation is much more pronounced in the rest of the molecules.

The dibenzo[ac]tetracene dication ($3^+$) and its heterocyclic analogue tribenzo[ac]phenazine dication ($4^+$) 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 $^{13}C$/$^1H$ correlation spectroscopy 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" and the "phenazine" 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 $C_{15a}$, $C_{10b}$ of the negatively charged part of dibenzo[ac]-tetracene dication ($3^+$) accommodate relatively high positive charges. Positions $C_{10a}$ and $C_{15b}$ 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 atoms between them and affect the charge alternation. Indeed $C_{9b}$ and $C_{14b}$, the starred carbons between these two unstarred carbons ($C_{10b}$ and $C_{15a}$), absorb at $150.9$ ppm which is the lowest absorption band found in the $^{13}C$ spectrum of $3^+$ (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 carbons $C_{15a}$ and $C_{16a}$ atoms which again are between two unstarred and highly negatively charged carbons $C_{10a}$ and $C_{15b}$, respectively.

In the benz[c]cinoline dianion ($5^-$) and the tetracene dication ($6^+$) the charge alternation operates well in the entire system. The benz[c]cinoline dianion ($5^-$) which is the heteroanologue of phenanthrene dianion ($1^+$) has a charge distribution similar to that of $1^+$. The same division can be made into fragments with the nitrogen atoms placed in positions that accommodate much negative charge. Tetracene dication $6^+$ behaves like $2^+$ 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 the results of the dication $7^+$ and the dianion $8^-$ are shown separately (Figure 2), and we chose to concentrate on the dianion which has recently been reexamined. 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 $7^+$ (Figure 2). Compare, for example, the charge density and the $^{13}C$ NMR bands of the $C$ and $H$ which are nonstarred carbon atoms ($-0.069$ and $141.8$ ppm, respectively) with their two starred neighbors $C_{15a}$ and $C_{16a}$ ($-0.222$ and $93.3$ ppm, respectively). The quaternary nonstarred neighbors of $C_{15a}$ accommodate only $-0.083$ units of charge and absorb at low field ($149.2$ ppm), while the starred atoms $C_{15b}$ and $C_{16b}$ 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 $7^+$ as well as in $7^+$ appears at the central carbons $C_{5b}$ and $C_{6b}$. 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 $C_{5b}$ and $C_{6b}$ deviate demonstrates that the origin to these deviations are not the results of anisotopic effects only, so that the search for real electronic factors affecting these deviations. Calculation predicts that the HOMO of pyrene dianion ($7^+$) has a node through carbons $C_{2b}-b_{10b}$ 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 $C_{5b}$ and $C_{6b}$ 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.

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 $8^-$ can be divided by a plane of symmetry bisecting $C_{14}$ and $C_{15}$ 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 dication ($2^+$) or dication ($2^+$) and tetracene dication ($6^+$) for the same reasons. It should be noted that in the systems $8^-$, $8^+$, $9^-$, $10^-$ and $10^{2-}$ 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 $11^-$ is distributed over the entire periphery, which is in line with a previous report that acenaphthylene dianion ($1^+$) can be regarded as an annulene with a [13]perylene (13C) periphery. However, the calculated charge densities and the experimental charge alternation concept works nicely although these compounds have more complicated structures (Figure 4). The charge in $11^-$ is distributed over the entire periphery, which is in line with a previous report that acenaphthylene dianion ($1^+$) can be regarded as an annulene with a [13]perylene (13C) periphery. However, the calculated charge densities and the experimental
distributions explain the selective protonation of Am. Chem. Soc., Vol. 110, No. 14, 1988

Figure 4. Calculated charge densities and $^1$C NMR chemical shifts ($\Delta \delta^1$C or $\delta^1$C) ofacenaphthylene dianion (11$^-$) and related systems (see text).

The charge density on carbons $C_1$ and $C_2$ of 11$^-$ is therefore lower than expected after bisection of the molecule across the $C_1$-$C_2$ bond and along the $C_{5a}$-$C_8$ bond. Most of the charge is at positions $C_9$ and $C_{10}$ rather than at $C_1$ and $C_2$. 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$^-$ at $C_{5a}$ in a mixture of THF/NH$_3$.2b

In the case of acephenanthrylene dianion (12$^-$) 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,21,22 and charge alternation generally prevails in the acephenanthrylene dianion (12$^-$) as well as in fluoranthene dianion (13$^-$)$^3$ (see Figure 4). In 11$^-$ and 12$^-$ there is a clear disagreement between the experimental shift (1$^3$C) 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$^-$ and 13$^-$ is manifested by the HOMO's of these dianions which has 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 space charge alternation mechanism, may be operative as suggested for the central bond of the pyrene dianion (7$^-$).

In the isoprene dianion (14$^-$)$^3$ 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

(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, J. M. J. Org. Chem. 1987, 52, 4207. (b) Muller, 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. S.; Huber, W.; Schneiders, C.; Mullen, K. Chem. Ber. 1983, 116, 1575. Calculated charge densities given for 12$^-$ were obtained from $\omega$ calculations (this work).

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$^-$ and 17$^+$)$^2$ that were investigated recently by modern NMR techniques which enable unambiguous assignment of their simple carbon spectra. The biphenylene dianion (17$^-$) was shown to be diatropic with a very high proportionality constant ($K_c$) of 174 ppm per electron.24

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

of starred carbons C8 and C4 are shifted to high field by 37.2 ppm to obtain information on the bond length of the azulene dianion. For example, the starred carbon C6 is shifted by 69 ppm to high field; C4a and C8b are shifted to high field by 11.1 ppm. The next pair of carbons of that do not behave as expected according to the charge alternation concept are the quaternary carbons C4a:9a and C4b: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 C3 is shifted by 69 ppm to high field; and its calculated charge density is -0.44 units of charge. Its nonstarred neighbors C1 and C5 have a positive charge +0.04 units each and are shifted to downfield by 11.1 ppm. The next pair of starred carbons C3 and C5 are shifted to high field by 37.2 ppm.


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 C4a-C8b and C4b-C8a 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^+. 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 C1a and C2a.25 Although the calculation gave higher charge density at the starred atoms C1a, the differences in the carbon chemical shift Δδ^{13}C is larger for C2a (12 ppm compared with 6.0 ppm for C1a). 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 C4a:9a and C4b: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 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 ^13C chemical shift. The agreement between the calculated charge densities with the I3C chemical shifts of the nonstarred carbon C1a, C2a, and C5, 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 pentadienylic anion connected by two "virtually single bonds". In each substructure the charge alternation prevails in a very pronounced way.

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

Johann Mulzer, Ulrich Steffen, Ludwig Zorn, Christian Schneider, Elmar Weinhold, Winfried Münch, Rainer Rudert, Peter Lugger, and Hans Hartl

Contribution from Institut für Organische Chemie der Freien Universität, Takustrasse 3, D-1000 Berlin 33, FRG. Institut für Kristallographie der Freien Universität, Takustrasse 6, D-1000 Berlin 33, FRG, and Institut für Anorganische Chemie der Freien Universität, Faberstrasse 34-36, D-1000 Berlin 33, FRG. Received August 7, 1987

Abstract: The enolates 4a,b obtained from ester 3a on deprotonation with lithium disopropylamide in THF and THF/HMPA, respectively, add alkyl halides and benzaldehyde with 99% diastereoselectivity to form 3-f. The structure of 3b was established by X-ray crystallography via the corresponding 5,6-diol 31. This unusually high chirality transfer is not due to a chelate-controlled mechanism, as the partially deoxygenated derivatives 9d, 10d, and 11e show the same as 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.

Chirality may be incorporated into ester enolates by means of the alkoxy-ribosyl (C-ribosyl) (or C-ribosyl) component. In either case, efficient stereocontrol of electrophilic additions to a prochiral ester carbon may be exerted by chelate-enforced chirality transfer, particularly in chelate rings of sizes 5-7. In contrast to the configurationally unrestricted O-ribosyl case, chelate formation in C-ribosyl ester enolates requires E geometry around the double bond. This demand contradicts Ireland’s rule, according to which Z-enolates are generated with high diastereoselectivity. However, the same is true for the Z-enolate axial attack of 3d, which shows 99% diastereoselectivity. The X-ray and NMR data for 3b confirm the structure of 3-f, and the chirality transfer is ascribed to a frontside attack of the ester enolate 3b on the C-ribosyl model compound 21a-d.