Tetrahedron Vol. 41, No. 4, pp. 785 to 791, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

PARATROPICITY AND ANTIAROMATICITY: ROLE OF THE HOMO–LUMO ENERGY GAP

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(*Received in UK 5 January 1984*)

Abstract—Doubly charged systems derived from fused benzenoid polycycles reveal an unquenched delocalization of 4 n π-electrons and hence are predicted to possess antiaromatic character. The magnitude of the paratropic ^{1}H NMR chemical shifts, due solely to the paramagnetic secondary field sustained in these species, was found to depend linearly upon the magnitude of LUMO–HOMO energy gaps of the corresponding systems. The existence of such a correlation enables a comprehensive treatment of the various factors which determine the antiaromatic character and the subtle interrelations between those factors. This, in turn, leads to a deeper understanding of antiaromaticity.

INTRODUCTION

An outstanding achievement of molecular orbital theory was Hückel's prediction[1] that conjugated monocyclic systems containing (4 n + 2) π-electrons should be aromatic, i.e. conjugatively stabilized.[2] This proposition was modified by Platt to encompass neutral as well as charged polycyclic systems with (4 n + 2) π-electrons in the path of conjugation.[3] Cyclic polyenes which did not fit the (4 n + 2) rule, and indeed did not reveal a conjugative stabilization, were generally classified as "pseudoaromatic" until 1965, when Breslow coined the term "antiaromaticity".[4] This term was meant to connote and emphasize a significant destabilization characteristic of certain 4 n π-conjugated monocycles, such as cyclobutadiene and cyclopropyl anion.[5] In agreement with Breslow's observation, theoretical calculations led to the estimation of negative conjugation energies—at least in the two mentioned species.[6]

Hückel's theory initiated a wealth of experimental work, all of which fitted with the prediction of enhanced stabilization in (4 n + 2) π-systems. The measure of variegated physical and chemical quantities (such as heats of combustion and hydrogenation, magnetic susceptibilities, electronic spectra and the proclivity to react in Diels–Alder reactions) was found to correlate with the extent of aromatic character, as estimated by the theoretical methods.[2]

The experimental support for antiaromaticity is far less satisfactory. The inherent instability of antiaromatic systems, rationalized by their high energy content, results in a complete failure to isolate these compounds. Consequently, the possibility of corroborating theoretical predictions for systems in this elusive class through confrontation with experiment, is disturbingly limited. Even more so, any attempt theoretically to estimate the relative magnitude of antiaromatic character in 4 n π-systems and then correlate this estimation with an experimental parameter, was hitherto bound to suffer from lack of support by such experimental data.

In the quest for such a correlation, we examine the magnitude of the anisotropic paramagnetic susceptibilities, known to characterize 4 n π-cyclic conjugated systems, by means of their effect upon ^{1}H NMR chemical shifts. The magnitude of this effect was then examined as a function of the energy gap between the lowest vacant (LUMO) and the highest occupied (HOMO) molecular orbitals of the corresponding systems. The rationale for such an inspection is the allegation that antiaromaticity is a particular aspect of antibonding;[5] if so, the proximity of excited, antibonding, states to the ground state, and consequently, their exerted effect upon it, is expected to be directly related to the antiaromatic character of the system. NMR measurements have an obvious advantage over other techniques, as the unstable antiaromatic species may be prepared from suitable, stable precursors, and studied in the reaction vessel, i.e. in the NMR tube.

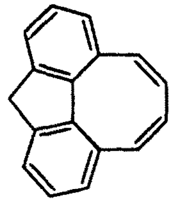
For reasons to be discussed, we chose doubly charged polybenzenoid molecules as model compounds for antiaromaticity. Our studies point towards the existence of a direct, unequivocal correlation, between the extent of paratropicity experienced by the antiaromatic systems, and the corresponding LUMO–HOMO energy gap, as estimated by SCF–MO calculations.

ANTIAROMATICITY—DISCUSSION

Antiaromaticity—as well as aromaticity—represent primarily a state of energy. Therefore, a parameter which directly reflects the energy content of antiaromatic systems, or more specifically, the extent of destabilization due to antiaromatic character, seems to be a most suitable choice. Yet, methods designed to estimate the extent of this destabilization are inherently problematic in the same sense that methods aimed at the evaluation of aromatic stabilization remain ambiguous.[2] At the crux of the problem lies the observation that the notion of conjugative stabilization or destabilization is, by definition, relative, and therefore requires reference systems that are devoid of cyclic delocalization. When aromatic systems are considered, the various methods designed to estimate the measure of the conjugative energy stabilization[7-10] generally agree.[11] This is hardly the case when antiaromatic contributions are expected; here the estimated magnitudes of the resulting destabilization differ substantially. The estimated extent of destabilization due to antiaromaticity is not only sensitive to the choice of reference compounds, but is also highly susceptible to the level of sophistication of the quantum chemical calculation.[6a,12] Thus, the simple HMO treatment assigns nonaromatic character to cyclobutadiene if two isolated double bonds constitute the reference system, while inclusion of overlap in HMO or in SCF–MO calculations leads to the prediction of antiaromaticity, i.e. to the estimation of negative resonance energy.[5] In view of these theoretical uncertainties, and since the measure of resonance energies is virtually impossible in antiaromatic systems, we had to look for other theory-based indices.

While the $(4n + 2)$ π-annulenes are predicted by HMO to have all π-electrons paired in bonding MO's, the $4n$ π-class is estimated to possess two unpaired electrons in two degenerate nonbonding molecular orbitals.[2a,13] On passing to SCF–MO methods, where allowance is made for effects of electron repulsion, orbital degeneracy is retained by symmetry, but the triplet and singlet configuration are no longer degenerate. Still, the first excited singlet state remains very close to the triplet ground state, and results in a pseudo Jahn–Teller distortion in $4n$ π-annulenes, characterized by bond-length alternation and severe deviation from coplanarity.[14] Thus, in systems such as cyclooctatetraene or [12] annulene an effective cyclic delocalization is ruled out and consequently these species cannot be labelled as antiaromatic. A rather different situation occurs in polycyclic systems. The rigidity imposed by inner bonds reduces substantially the extent of bond-length alternation or the deviation from planarity. This outcome is observed in cycloocta[*def*]fluorene (**1**)[15] or in the pyracylene system (**2**),[16] which, in Platt's peripheral approach, represent [16] and [12] perturbed annulenes, respectively. In contrast to the monocyclic systems, these $4n$ π-species, being planar with approximately constant bond lengths, are predicted to reveal antiaromatic contributions. Yet, due to the reduced symmetry in these polycycles, relative to the hypothetical planar C_nH_n annulenes of D_{nh} symmetry, the degeneracy of the highest occupied molecular orbitals is removed and, consequently, the triplet configuration is no longer a ground state. However, the LUMO–HOMO energy gap, or the energy splitting between the singlet ground state and the excited triplet state, is much smaller than in monocyclic $4n$ π-systems. The diminution of geometrical distortion in the polycycles, when compared with the monocyclic series, is emphasized in polybenzenoid systems. Unless a large steric perturbation exists, the highly rigid benzenoid skeleton is bound to enforce planarity and approximate constancy in bond lengths not only in the neutral, but also in the doubly charged ions—dications and dianions—derived from the fused benzenoid systems. Thus, such doubly charged species seem to meet all the requirements imposed by the peripheral electronic model for antiaromaticity: they are $4n$ π-systems, in which, due to the suitable geometry, the peripheral delocalization of π-electrons is quite unperturbed. Moreover, in contrast with the neutral systems **1** and **2** where aromatic contributions of the benzenoid moieties are expected, the doubly charged polybenzenoid ions should reveal a "pure" antiaromatic character.

The predicted increase of the antiaromatic character, in doubly charged $4n$ π-polybenzenoids, is therefore directly related to a marked decrease in geometric distortion, that is, deviations from planarity and severe bond length alternation. This is clearly indicated by experimental data (*vide infra*). The decrease in geometric distortion is related, in turn, to a larger perturbance of a triplet configuration to the singlet ground state—as this excited triplet lies closer to the ground state configuration.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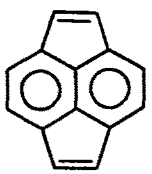
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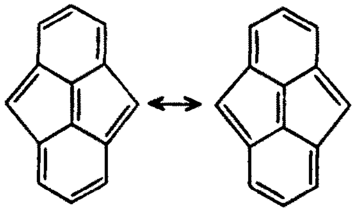

3a 3b

3

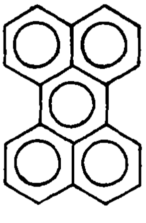
Consequently, a connection is pointed out between the extent of antiaromaticity and the increase in perturbance due to the triplet state. This is an observation of crucial importance and its exemplification is of basic interest. Computations at various levels of sophistication predict the lowest electronic transition of the $4n$ π-cyclooctatetraene to involve a π–π^* transition, and estimate its energy to be more than 4.0 eV.[17] This rather large energy is rationalized in terms of the geometrical distortions which characterize the COT system, leading to a quenching of any antiaromatic contribution. SCF–MO calculations performed on the polycyclic pyracylene (**2**) indicate that its lowest lying triplet configuration is approximately 2.05 eV above the singlet ground state.[16] The gap between the lowest triplet and the singlet states estimated for the dibenzopentalene (**3**) is only 0.23 eV.[16] The dissimilarity of the two perturbed [12] annulenes, **2** and **3**, is suggestive. System **2** might be depicted as an aromatic naphthalene core perturbed by two double bonds which are connected to the aromatic moiety by long, virtually single, bonds. The alternation of bond lengths results in a quench of the peripheral $4n$ π-antiaromatic contribution. In obvious contrast, when **3** is considered, no structure with a Kekulé ring can be drawn, thus no aromatic contribution is expected. Even more so, the two canonical forms **3a** ↔ **3b** imply a diminution in bond length alternation. Doubly charged $4n$ π-benzenoid polycycles exhibit disturbances from a triplet ground state which are estimated to correspond to 0.8–1.8 eV. Indeed, in a previous study[18] we have demonstrated, by means of NMR and ESR methods, that such doubly charged antiaromatic compounds possess a low lying, thermally accessible triplet state which allows the existence of an equilibrium process with the singlet ground state. NMR and ESR lineshapes were shown to depend on the extent and direction of this singlet–triplet equilibrium which, in turn, was found to be determined solely by the width of the energy gap between the LUMO and HOMO.

On grounds of the observations we conclude that *the extent of perturbance from triplet ground state of a 4n π-conjugated compound, cyclic or polycyclic, constitutes a plausible index for the assessment of antiaromaticity.* As a theoretical approach, this is a quantitative index, since it is related to the energy splitting between the LUMO and HOMO of the antiaromatic system.[19] We also conclude that doubly charged benzenoid polycycles—dications and dianions—constitute appropriate model systems for antiaromaticity.

Among the experimental methods established for the estimation of aromatic, or antiaromatic character, the most frequently employed are measures of properties that are related to sustained magnetic phenomena.[12,14,20] These phenomena represent the outcome of two different contributions: the diamagnetic contribution due to Larmor precession of π-electrons around the ring which depends only on electron density in bonding molecular orbitals—an exclusive ground state property. In contrast, the second, paramagnetic, contribution depends on electronically excited states, since it reflects magnetic dipole transitions between occupied and vacant molecular orbitals.[14,21a] Obviously, such transitions would be particularly favored when the system possesses a low-lying excited state, or, in other words, when the energy separation between the LUMO and HOMO is small.[21] A relation between the experimental consequences of a paramagnetic secondary field and the theoretical concept of antiaromaticity depends on the LUMO–HOMO gap, becoming both more pronounced as this gap narrows. One should note that the dependence of antiaromaticity and the paramagnetic term upon the energy gap is not a mere correlation: *both properties originate directly from a narrow LUMO–HOMO energy gap.*

A readily observed result of the secondary paramagnetic field is a paratropic, high-field shift which characterizes the ^{1}H NMR absorptions of antiaromatic species. However, the information obtained from these high-field shifts was hitherto strictly qualitative and in most cases open to controversy and ambiguity.[12] This, again, is due to the scarcity of systems that reveal pure or even substantial antiaromatic contributions and, even more so, to the lack of antiaromatic homologous series. Doubly charged benzenoid polycycles seem to provide the sole example of a relatively large 4n π-series in which the various compounds differ either in topology or in the number of π-electrons (i.e. the value of n), and none of them presents a difficulty due to a perturbed delocalization.

The oxidation of ten polycyclic benzenoid hydrocarbons (**4**–**13**) was carried out by the reaction of the neutral compounds with a SO_2ClF solution of SbF_5 which, being a very strong Lewis acid, acts as a powerful oxidizing agent.



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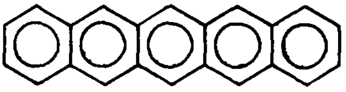

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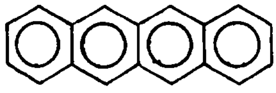

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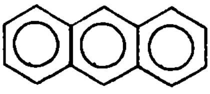

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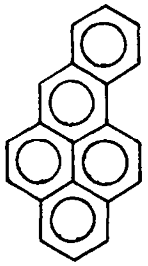

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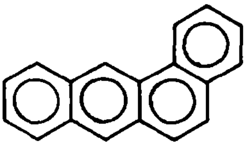
The ^{13}C NMR spectrum of each of the various samples revealed a substantial total low-field shift which amounts to *ca* 200–250 ppm relative to the neutral hydrocarbon. These diamagnetic shifts demonstrate the formation of dications, since ^{13}C NMR absorptions are highly sensitive to charge densities, and only to much lesser extent, to the effect of ring currents.[22,23] As for the ^{1}H NMR patterns, they are determined by two factors which are expected to operate in opposite directions: deshielding due to the positive charge density, and shielding caused by the induced paramagnetic secondary field.[22]

We used SCF–MO calculations[24] as a means to assess the portion of chemical shift that is due to the charge density factor and isolate thereby the contribution of the paramagnetic ring current. In each of the charged species, the theoretical charges on hydrogen-bearing carbon atoms were summed, and this sum was multiplied by the shift–charge correlation constant (10.7 ppm).[23] The product was then divided by the number of protons in order to obtain an average value of deshielding due solely to the positive charge density. This average was added to the center of gravity of the ^{1}H NMR chemical shifts exhibited by the neutral polycyclic hydrocarbons. An estimate of a theoretical center of gravity in the absence of secondary fields is thus derived. An observed high-field deviation from this estimate can therefore be taken as evidence for and a measure of the antiaromatic, paramagnetic contribution.



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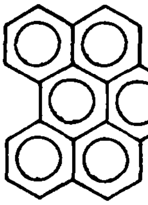

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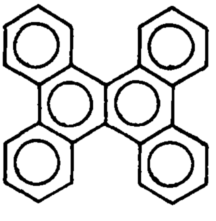

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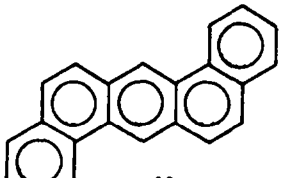

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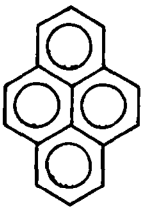

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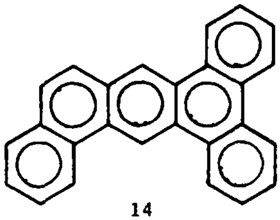

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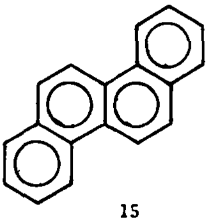

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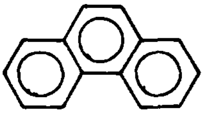

16

The reduction of nine polycyclic catacondensed benzenoid hydrocarbons (i.e. **5**–**7**, **9**, **11**, **12**, **14**–**16**) to the corresponding dianions was performed by exposing the tetrahydrofuran solutions of the neutral systems to lithium or sodium metals.[25] ^{13}C NMR spectra, obtained after four to six days of exposure to the metal revealed the expected paratropic shifts due to the shielding of two negative charges.[23] The ^{1}H NMR patterns of the dianions are determined mainly by the same two factors which influence the absorption revealed by the dications. Yet, in this case the two factors operate in the same direction. The two negative charges result in a shielding effect which causes a high-field shift, the magnitude of which is now increased due to the effect of the induced paramagnetic secondary field. The net contribution of this paramagnetic effect is thus calculated in the dications, and the average effect of the negative charge density is now subtracted from the center of gravity of the ^{1}H NMR chemical shifts of the neutral molecule. The extent of the paratropic shift beyond this estimate is taken as the pure contribution of the antiaromatic paramagnetism. A correlation between the value of LUMO–HOMO energy splittings and the paratropic shift due solely to the secondary field, analogous to the correlation established by the dications, is obtained.

RESULTS AND DISCUSSION

When the ^{1}H NMR chemical shifts of the dications obtained by twofold oxidations of systems **4**–**13** were processed as described, the various charged systems revealed substantially different paratropic deviations ($\Delta\delta$ values in Table 1). While species such as the pyrene (**13**) and the dibenzanthracene (**12**) dications exhibited large high-field shifts, relative to the values expected by charge-density considerations, the paratropic shift deviation in the pentacene (**5**) dication was much smaller. We found that the extra paratropic shifts display an unequivocal correlation with the calculated energy gap between lowest unoccupied and highest occupied molecular orbitals of the 4 n π-antiaromatic dications (Table 1, Fig. 1): when a large split is estimated, a small paratropic shift is observed, and *vice versa*. When the relationship between this energy gap and the net paratropic shift is approximated as linear, regression analysis (excluding the pyrene dication) yields:

$$\Delta\delta(\text{ppm}) = -1.23\ G\ (\text{eV}) + 4.31$$

$$(\pm 0.13\ \text{ppm, correlation coefficient } 0.984) \qquad (1)$$

where G is the computed gap.

As for the dianions (Table 2, Fig. 2), the regression analysis (excluding phenanthrene dianion) yields:

Table 1. ^{1}H NMR Paratropic shifts of polybenzenoid dications vs LUMO–HOMO energy gaps

System[a]	Neutral systems; exptl. ^{1}H NMR center of gravity[b]	Overall diatropic shift[b,c]	Charged systems; calc. ^{1}H NMR center of gravity[b,c]	Charged systems; exptl. ^{1}H NMR center of gravity[b,c]	$\Delta\delta$ Calc.-exptl.[b,c]	Calc. LUMO-HOMO gaps[c,d]
4	7.95	1.80	9.75	8.61	1.14	2.512
5	8.08	1.90	9.98	8.61	1.37	2.252
6	8.01	2.12	10.13	8.60	1.53	2.219
7	7.90	2.53	10.43	8.39	2.04	1.903
8	7.91	1.67	9.58	7.33	2.25	1.782
9	7.86	1.71	9.57	6.85	2.72	1.445
10	8.20	1.48	9.68	6.88	2.80	1.308
11	8.28	1.14	9.42	6.41	3.01	0.926
12	8.14	1.56	9.70	6.51	3.19	0.817
13	8.21	2.41	10.62	5.95	4.67	2.838

[a] For numbering - see text. [b] PPM down from $SiMe_4$. [c] For computation details see text. [d] eV units, as furnished by SCF-MO method.

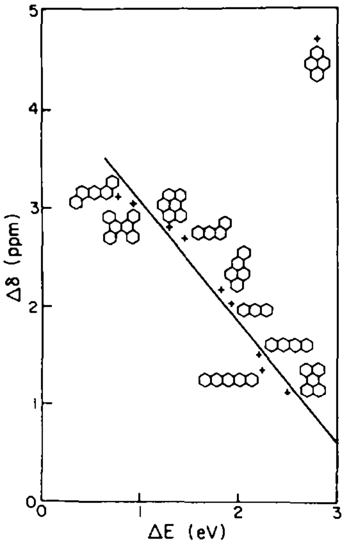

Fig. 1. ¹H NMR paratropic shifts of 4 n π-polybenzenoid dications vs LUMO–HOMO energy gaps.

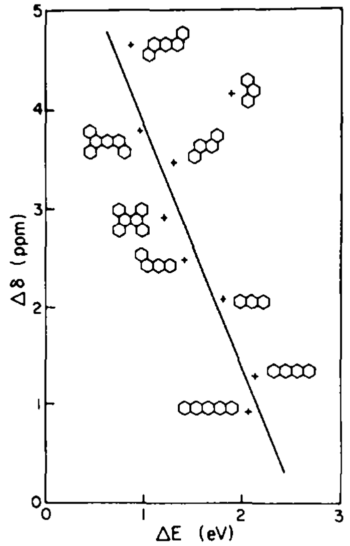

Fig. 2. ¹H NMR paratropic shifts of 4 n π-polybenzenoid dianions vs LUMO–HOMO energy gaps.

$$\Delta\delta(\mathrm{ppm}) = -2.50\,G + 6.40$$

$$(\pm\ 0.32\ \mathrm{ppm,\ correlation\ coefficient}\ 0.953) \qquad (2)$$

Again, it is found that a large LUMO–HOMO gap is related to small paratropic shifts and vice versa.

The correlation coefficients in both relationships substantiate a monotonous, perhaps even linear, interdependence, between the extent of the LUMO–HOMO splitting and the magnitude of the paratropic chemical shift. Yet, when the two correlations are compared, differences in their pattern stand out. The correlation for the dications is better than that for the dianions. Also, the slope of the line exhibited by the dianions is larger than the slope for dications (−2.50 vs −1.23, corresponding to −68.2° and −51.0°, respectively). In other words, the dependence of the paratropic shifts upon the LUMO–HOMO gaps is more emphasized in the negatively- than in the positively-charged systems. The larger deviations from a linear correlation in the dianions, as well as the larger slope, can be rationalized in terms of the states of solvation of the salts, and the influence of these states upon the molecular structure of the organic ions. As already mentioned, benzenoid dianions, being antiaromatic and thus possessing narrow LUMO–HOMO gaps, undergo an equilibration between a singlet ground state and a low-lying, thermally accessible triplet state.[18] Conditions which favor tight contact ions[26] (large alkali cations, elevated temperatures, solvent with low solvating power) shift this singlet–triplet equilibrium towards the triplet through a further reduction of the LUMO–HOMO gap, and therefore results in an enhanced NMR line broadening.[18]

The dependence of NMR patterns upon states of solvation is revealed only by the dianionic benzenoid polycycles and not by the analogous dications. This is rationalized by a very efficient solvation of the

Table 2. ¹H NMR Paratropic shifts of polybenzenoid dianions vs LUMO–HOMO energy gaps

System[a]	Neutral systems; exptl. ¹H NMR center of gravity[b]	Overall paratropic shift [b,c]	Charged systems; calc. ¹H NMR center of gravity[b,c]	Charged systems; exptl. ¹H NMR center of gravity[b,c]	Δδ Calc.-exptl.[b,c]	Calc. LUMO-HOMO gaps[c,d]
5	8.08	2.17	5.91	4.98	0.93	2.070
6	8.01	2.50	5.51	4.23	1.28	2.133
7	7.90	2.76	5.14	3.06	2.08	1.833
9	7.86	2.15	5.71	3.22	2.49	1.411
11	8.28	1.18	7.10	4.18	2.92	1.205
12	8.14	1.70	6.44	1.78	4.66	0.884
14	8.43	1.23	7.20[e]	3.51	3.69	0.990
15	7.80	1.90	5.90	2.42	3.48	1.333
16	7.67	2.32	5.35[e]	1.18	4.17	1.898

[a] For numbering - see text. [b] PPM down from $SiMe_4$. [c] For computation details see text.

[d] eV units, as furnished by SCF-MO method. [e] Unresolved, broad NMR absorptions.

inorganic counter anion in the media[27] which results in an almost total shielding of the organic dications from effects exerted by the counter anions. The difference in the extent of influence exerted by the counter ions upon antiaromatic dications vs dianions provides an interpretation of the observed differences between the correlations.

The influence of the counter cations upon the dianions, though unaccounted for by the SCF–MO calculation, is supposed to vary from one system to another. The varying magnitude of this influence is due to the different extent of interaction between the dianions and their counter cations, caused, in turn, by the different topologies and modes of electron delocalizations (and hence electron densities) of the various 4 n π-conjugated polycycles. We believe that the larger deviations from a linear dependence (and hence the lower correlation coefficient) revealed by the dianions, is the manifestation of these variations. The second dissimilarity between the two relationships, i.e. the larger slope exhibited by the dianions, can also be rationalized in terms of the emphasized influence of counter cations upon the antiaromatic dianions. As already pointed out, this influence is a result of the narrowing of the LUMO–HOMO energy gap due to the larger increase in energy of the highest occupied relative to the lowest vacant orbitals. This effect is assumed to be operative in all the dianions, but their *relative* outcome is assumed to depend on the initial magnitude of the LUMO–HOMO gaps. In those antiaromatic dianions where skeletal topology imposes large energy gaps, the narrowing is negligible relative to the overall energy splitting. This is to be contrasted with dianions that are characterized by initial small gaps, in which any narrowing due to counter cations is supposed to be relatively significant and responsible for pronounced effects. Consequently, all the systems which are, *a priori*, "more antiaromatic" in the sense of having a small frontier orbital separation, and thus appear at the upper part of the correlation line (e.g. dibenzanthracene and dibenzochrysene dianions in Fig. 2), are more susceptible to mechanisms which act to enhance the antiaromatic character. This results in larger paratropic ^{1}H NMR shifts and hence, in a larger slope.

The rather good correlation coefficient revealed by the two plots (eqns 1 and 2) seems to present, by themselves, an indirect justification of the assumptions included in the theoretical approach. However, theoretical calculations based upon totally different considerations and intended to estimate delocalization energies in dianions, point towards a general trend which is similar to our results. It has been shown[28] that the dianion derived from naphthacene (**6**) is "more" aromatic than the benzanthracene (**9**) dianion and therefore "less antiaromatic," while $\mathbf{9}^{=}$ is "less antiaromatic" than the doubly charged chrysene ($\mathbf{15}^{=}$). In the C_{20} series the dicarbanion derived from the dibenzanthracene (**12**) is estimated to be "more antiaromatic" than the pentacene (**5**) dianion. This parallelism strengthens our chain of premises and even more so, it points towards a direct, quantifiable method to measure the LUMO–HOMO energy gaps of planar carbocyclic systems by means of their ^{1}H NMR paratropic chemical shifts.

The points for the pyrene (**13**) dication and phenanthrene (**16**) deviate significantly from the correlation lines. The reason for these deviations is not yet clear, but some possibilities come to mind: the effect of the σ core upon the π orbitals of these two species may differ in sign or magnitude from the corresponding influence exerted in the other systems. It seems that more refined calculations which include the σ core may shed light upon those few cases that do not fit the relationships, pointing at subtler effects to which the antiaromaticity phenomenon is susceptible.

CONCLUSIONS

Cyclic, or polycyclic systems in which an efficient, unquenched delocalization of 4 n π-electrons exists, and hence predicted to possess an antiaromatic character, are known to reveal paratropic ^{1}H NMR chemical shifts. The present study points to the existence of an unequivocal correlation between the magnitude of these paratropic shifts and the estimated widths of the HOMO–LUMO energy gaps in the antiaromatic species.

Our experimental parameter—the paratropic ^{1}H NMR chemical shift—is an outcome of an anisotropic paramagnetic field which is assumed to be sustained in 4 n π-antiaromatic cyclic or polycyclic conjugated systems. This field results, in turn, from a relatively large contribution of excited states to the ground state.[29] Such a contribution depends primarily upon the width of the splitting between the lowest vacant and the highest occupied molecular orbitals—it increases as the gaps decrease. "Pure" antiaromatic species are expected to reveal a triplet ground state, with one electron in each of two (highest occupied) orbitals. In polycyclic 4 n π-systems such as the doubly charged benzenoid compounds, the HOMO's degeneracy is removed, thus resulting in a singlet configuration. However, the LUMO–HOMO energy splitting is still narrow enough to enable a significant contribution of the excited states and therefore to characterize antiaromatic systems.

The very existence of a correlation between the paratropic ^{1}H NMR chemical shift and the theoretically evaluated LUMO–HOMO gaps provides a proof of this hitherto vague chain of premises related to antiaromaticity, as well as a possible scaling of its extent according to the energy gaps.

EXPERIMENTAL

The neutral polybenzenoids were purchased from Aldrich and recrystallized before use from EtOH or toluene.

The dianionic species were prepared by reduction of the respective neutral compound with sodium or lithium. The metal wire 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 sealed under vacuum. By turning the tube upside down, the solution was brought into contact with the metal wire. Detailed ^{1}H NMR spectra appear in a previous publication.[18]

The dicationic systems were prepared by introducing the solid neutral hydrocarbon to a 5 mm NMR tube containing SbF_5–SO_2ClF 1:1 solution which was kept in $-40°$ and stirred vigorously. A sealed capillary containing acetone-d_6 was then introduced and the tube was sealed.

For ^{1}H NMR parameters of the dications derived from anthracene (**7**) and naphthacene (**6**) see Ref. 30. The other dications revealed the following parameters:

perylene(**4**) *dication*: δ 9.20 (H_1, d, 4H, J = 8.2 Hz); 8.79 (H_3, d, 4H, J = 6.2 HZ); 7.88 (H_2, dd, 4H, $J_1 = 8.2$, $J_2 = 6.2$ Hz).

pentacene (**3**) *dication*: δ 9.29 (H_6, s, 2H); 9.00 (H_5, s, 4H); 8.26 ($H_{1,2,3,4}$, AA′BB′, 8H).

benzo[*a*]*pyrene* (**8**) *dication*: δ the charged system exhibits a complex spectrum; its chemical shifts range between 7.68 and 6.79 ppm. The center of gravity was obtained by averaging the chemical shifts and corresponding areas.

benz[*a*]*anthracene* (**9**) *dication*: δ 7.25 (H_5, d, 1H, J = 6.6 Hz); 7.17 (H_7, s, 1H); 6.93 (H_{12}, s, 1H); 6.98 (H_8, d, 1H, J = 6.6 Hz); 6.77–6.96 ($H_{8,9,10,11}$, 4H, ABCD pattern); 6.38–6.59 ($H_{1,2,3,4}$, 4H, ABCD pattern).

benzo[*ghi*]*perylene* (**10**) *dication*: δ 7.42 (H_3, d, 2H, J = 8.2 Hz); 7.33 (H_4, d, 2H, J = 7.6 Hz); 7.33 (H_1, d, 2H, J = 7.5 Hz); 6.64 (H_2, H_5, m, 4H); 5.71 (H_6, s, 2H).

dibenzo[*g,p*]*chrysene* (**11**) *dication*: δ 6.93 (H_2, t, 4H, J = 7.2 Hz); 6.50 (H_4, d, 4H, J = 7.7 Hz); 6.26 (H_3, t, 4H, J = 7.7 Hz); 5.98 (H_1, d, 4H, J = 7.2 Hz).

dibenz[*a,h*]*anthracene* (**12**) *dication*: δ 7.02 (H_5, d, 2H, J = 7.1 Hz); 6.78 (H_2, t, 2H, J = 7.9 Hz); 6.95 (H_7, s, 2H); 6.44 (H_4, d, 2H, J = 8.4 Hz); 6.26 (H_1, d, 2H, J = 7.9 Hz); 6.30 (H_6, d, 2H, J = 7.1 Hz); 6.21 (H_3, t, 2H, J = 8.3 Hz).

NMR spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz and 75.46 MHz for ^1H and ^{13}C, respectively. The field/frequency regulation was maintained by ^2H locking. The FID signals were digitalized and accumulated on an Aspect-2000 computer (32K). All chemical shifts are reported relative to Me_4Si.

REFERENCES AND NOTES

[1] E. Hückel, *Z. Phys.* **70**, 204 (1931).

[2] For general reviews see: [a]P. J. Garratt, *Aromaticity*. McGraw-Hill, London (1971); [b]E. Clar, *The Aromatic Sextet*. Wiley-Interscience, New York (1972); [c]M. J. S. Dewar, *The M.O. Theory of Organic Chemistry*, pp. 152–190, McGraw-Hill, New York (1969); [d]F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, Part A, pp. 369–419. Plenum Press, New York (1977); [e]I. Agranat, *MTP Int. Rev. Sci.: Aromatic Compounds* **3**, 139 (1973).

[3] J. R. Platt, *J. Chem. Phys.* **22**, 1448 (1954).

[4] R. Breslow, *Chem. Engng News* **43**, 90 (1965).

[5] R. Breslow, *Accts Chem. Res.* **6**, 393 (1973).

[6a] N. L. Bauld, T. L. Welsher, J. Cessac and R. L. Holloway, *J. Am. Chem. Soc.* **100**, 6920 (1978); [b]R. D. Mitchell and N. L. Bauld, *Isr. J. Chem.* **20**, 319 (1980).

[7] M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.* **91**, 789 (1969).

[8a] B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.* **93**, 305 (1971); [b]B. A. Hess and L. J. Schaad, *Ibid.* **93**, 2413 (1971).

[9a] M. Randić, *J. Am. Chem. Soc.* **99**, 444 (1977); [b]M. Randić, *Chem. Phys. Lett.* **38**, 68 (1976).

[10a] I. Gutman, M. Milun and N. Trinajstic, *J. Am. Chem. Soc.* **99**, 1692 (1977); [b]P. Ilić, B. Sinkovic and N. Trinajstic, *Isr. J. Chem.* **20**, 258 (1980).

[11] R. C. Haddon, *J. Am. Chem. Soc.* **101**, 1722 (1979).

[12] R. B. Mallion, *Pure Appl. Chem.* **52**, 1541 (1980).

[13] R. Breslow, *Pure Appl. Chem.* **54**, 927 (1982).

[14a] R. C. Haddon, V. R. Haddon and L. M. Jackman, *Fortschr. Chem. Forsch.* **16**, 103 (1970); [b]M. Rabinovitz, I. Willner and A. Minsky, *Accts Chem. Res.* **16**, 298 (1983).

[15] I. Willner and M. Rabinovitz, *Nouv. J. Chim.* **6**, 129 (1982).

[16] B. M. Trost and P. L. Kinson, *J. Am. Chem. Soc.* **97**, 2438 (1974).

[17] F. Zuccarello, G. Buemi and A. Randino, *J. Comput. Chem.* **1**, 341 (1980).

[18a] A. Minsky, A. Y. Meyer and M. Rabinovitz, *Angew. Chem. Int. Ed. Engl.* **22**, 45 (1983); [b]A. Minsky, A. Y. Meyer, R. Poupko and M. Rabinovitz, *J. Am. Chem. Soc.* **105**, 2164 (1983).

[19] A. Minsky, A. Y. Meyer and M. Rabinovitz, *Tetrahedron Lett.* **23**, 5351 (1982).

[20a] L. Salem, *The M.O. Theory of Conjugated Systems*, pp. 206–220. Benjamin, New York (1966), and references cited therein; [b]J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.* 856 (1961); [c]C. A. Coulson and R. B. Mallion, *J. Am. Chem. Soc.* **98**, 592 (1976); [d]R. McWeeny, *Molec. Phys.* **1**, 311 (1958); [e]C. W. Haigh and R. B. Mallion, *Prog. NMR Spectrosc.* **13**, 303 (1980); [f]J. Aihara, *J. Am. Chem. Soc.* **101**, 5913 (1979).

[21a] H. C. Longuet-Higgins, *Aromaticity*, Chemical Society Special Publication, No. 21, p. 109. London (1967); [b]J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.* **88**, 4811 (1966).

[22] For general review see: R. N. Young, *Prog. NMR Spectrosc.* **12**, 261 (1978).

[23a] R. Schaefer and W. F. Schneider, *Can. J. Chem.* **41**, 966 (1963); [b]H. Spiesecke and W. F. Schneider, *Tetrahedron Lett.* 468 (1961).

[24] As the crystallographic data for the charged systems are not available, ωβ results were used as an input for the SCF computations.[24,25] [a]G. V. Boyd and N. Singer, *Tetrahedron* **22**, 3383 (1966); [b]J. A. Berson, E. M. Evleth and Z. Hamlet, *J. Am. Chem. Soc.* **87**, 2901 (1965); [c]A. Streitwieser, *ibid.* **82**, 4123 (1960); [d]A. Y. Meyer and J. Serre, *Theoret. Chim. Acta* 117 (1967); [e]A. Y. Meyer, *ibid.* **16**, 226 (1970); [f]A. Y. Meyer and R. Pasternak, *ibid.* **47**, 27 (1978).

[25] Early NMR studies of polycyclid dianions are reported: [a]R. G. Lawler and C. V. Ristagno, *J. Am. Chem. Soc.* **91**, 1534 (1969); [b]K. Mullen, *Helv. Chem. Acta* **59**, 1357 (1976).

[26] D. H. O'Brien, C. R. Russell and A. J. Hart, *J. Am. Chem. Soc.* **101**, 633 (1979).

[27] A. Commeyras and G. A. Olah, *J. Am. Chem. Soc.* **91**, 2929 (1969).

[28] R. B. Bates, B. A. Hess, C. A. Ogle and L. J. Schaad, *J. Am. Chem. Soc.* **103**, 5052 (1981).

[29] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, pp. 262–276. Oxford University Press, Oxford (1932).

[30] D. M. Brouwer and J. A. Van Doorn, *Rec. Trav. Chim.* **91**, 1110 (1972).