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ASPECTS OF CYCLIC CONJUGATION

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Abstract - (a) The usefulness of PMO theory as a guide to chemical behaviour is illustrated by its application to spiroconjugation. It is shown in this way that spiroconjugation can be chemically important only in the case of spiro [3,3] heptadieniyl which may be sufficiently stabilized to exist as a monomeric "nonclassical" species. (b) The resonance integral between two sp^3 AOs of a given carbon atom is at least as large as the $p\pi:p\pi$ resonance integrals in conjugated hydrocarbons. Paraffins are thus σ-conjugated molecules, isoconjugate with polyenes. Cyclopropane should, like benzene, be aromatic, and cyclobutane, like cyclooctatetraene, antiaromatic. The available evidence shows this to be the case. (c) Consistent failure to reproduce the aromatic structures of higher annulenes, by a variety of procedures, suggests strongly that some factor must be operating other than those responsible for aromaticity and antiaromaticity in small rings. MNDO studies indicate this to be a special type of electron correlation, analogous to that postulated by Löwdin in his alternant orbital theory.

INTRODUCTION

The purpose of this contribution is to consider some problems concerning molecules with various kinds of cyclic conjugation and the conditions under which presence of such conjugation leads to aromaticity and antiaromaticity. The term will be used in a modification of the original sense given to it by organic chemists, i.e. to imply that a molecule in question has a more negative heat of formation (i.e. is more stable) that would be expected by analogy with open chain analogs. We will also require this extra stability to be due to cyclic conjugation involving, in LCAO MO terminology, the cyclic overlap of AOs in a ring of atoms, each atom contributing one AO. This proviso is necessary to exclude cruciconjugated systems such as the phosphonitrile chlorides, a topic which has been discussed recently elsewhere. An antiaromatic compound is likewise one which is destabilized by cyclic conjugation.

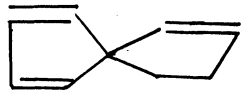
Theoretical problems of this kind can be treated at various levels, ranging from the simplicity of PMO (Ref.1) to sophisticated *ab initio* treatments. Here, as in most cases (Refs.1,2) PMO theory provides an excellent qualitative account of phenomena, generally superior and certainly simpler than those from simplistic calculations by procedures such as HMO or EH. Indeed, there is no point in carrying out calculations except by the most accurate and reliable procedures that are applicable to the system in question. While *ab initio* procedures are still far too inaccurate to be used in an *a priori* sense, calculations by use of Roothaan-Hall SCF MO method (Ref.3,4) with large basis sets seem in practice to give good results, especially if allowance is made for electron correlation by CI or in some other way. Unfortunately these procedures are limited by considerations of cost to rather small molecules, particularly if geometries are properly optimized - as they must be if the calculations are to be of chemical value. Simpler versions of the RH method, using small basis sets (e.g. STO-3G), are not sufficiently accurate while most of the semiempirical alternatives are very much worse, often leading to ridiculous results. For example, the EH method predicts

benzene to be unstable, dissociating without activation into acetylene, while CNDO predicts the most stable form of CO_2 to be a cyclic peroxycarbene, $\overset{O}{\diagdown C\diagup}$. The only exceptions at present are the semiempirical procedures we have developed, MINDO/3 (Ref.5) and MNDO (Ref.6), which seem to reproduce molecular geometries and energies with an accuracy comparable with those given by good ab initio methods and which can be applied with complete geometry optimization and at reasonable cost to quite large molecules. (Ref.7).

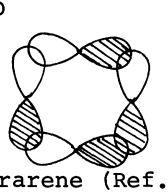
SPIROCONJUGATION

The idea that polyunsaturated spirans might show spiroconjugation through σ-type overlap of the two π systems was first suggested for the case of two interacting even conjugated systems by Simmons and Fukunaga (Ref.8), and for two odd ones by Hoffmann, Imamura, and Zeiss (Ref.9) in terms of orbital interactions between the two π systems. Our purpose here is to show how these compounds can be accommodated in the general theory of aromaticity given by PMO theory (Ref.10-12), this approach giving a rather more clear cut indication of the situations where spiroconjugation is likely to be significant.

The interactions between the two halves of such a spiran (e.g.(1)) are due to the types of orbital interaction indicated in (2), where the AOs ϕ_1 and ϕ_2 are the terminal 2p AOs in one π system while ϕ_3 and ϕ_4 are the terminal 2p AOs in the other. If the phases of the AOs in each π system are chosen to make all overlap positive, the phase relationships of the terminal AOs will be as shown in (2). It is then evident that while two of the interactions will involve positive overlap, two must involve negative overlap. The overall conjugated system that results therefore contains two phase dislocations (PD in (2))

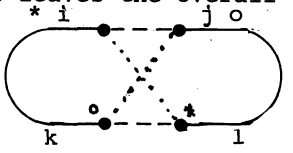


(1)



(2)

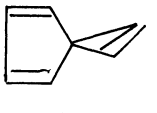
The composite conjugated system for a [m,n] spirarene (Ref.19) will then be isoconjugate with [m+n] annulene containing two bridges, linking the end of each m- or n-membered segment to the ends of the other. Two of these segments will involve phase dislocations. This situation is indicated in (3), the links without dislocations being indicated by dashes, those with dislocations by dots. (It is easily seen that inverting the phases of the AOs in one of the two segments leaves the overall situation unchanged).



(3)

First consider the case where m and n are both even. In this case atoms i and j (see(3)) will be of opposite parity (one "starred", the other "unstarred"; (Ref.9)) as will also be j and l. Two of the spiroconjugative interactions will therefore be between atoms of like parity and will have no first order effect on the total energy (Refs. 10-12). The other two will give rise to a (m+n) membered ring. If (m+n)=4k, this will be antiaromatic; if (m+n)=4k+2, aromatic. However, since the ring contains two very weak interactions, conjugated with the single bonds in each end segment, the bonds in the latter will alternate strongly. Any aromatic or antiaromatic effects should then rapidly diminish with ring size (Ref.11). It is indeed known that one weak homoconjugative interaction in benzene, leading to cycloheptatriene (4), virtually destroys the aromatic stabilization, so it is unlikely that any significant effects will be seen even in [4,2] spirarene (5). MINDO/3 calculations (Ref. 13) have shown that spiroconjugation leads to no change in total energy in the case of (1). The smallest spirarene, spiropentadiene (6), should be antiaromatic. However, it is likely in any case to be so strained that it may be difficult to distinguish between the two destabilizing factors.

(4)



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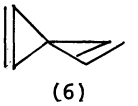
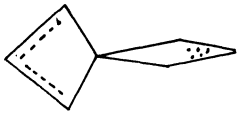


(6)

In the case where m and n are both odd, each segment of the spirarene is a radical. The heats of dimerization of conjugated radicals are ca 50 kcal/mole and dimerization requires no activation. Unless spiroconjugation leads to this degree of stabilization, such a compound will not therefore exist as a monomeric species, except perhaps in a matrix at low temperatures. Given that conversion to a tricyclic species (e.g.(7)→(8) is likely to take place unless the parent spirarene is quite strongly stabilized.



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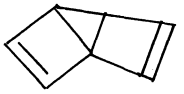
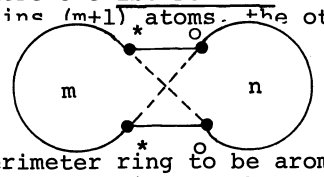


(8)

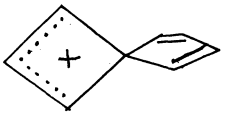
Following the line of argument indicated above, the spirarene will again be isoconjugate with a doubly bridged [m+n] annulene but this time the bridges link atoms of opposite parity and are therefore active. The spirarene is therefore isoaromatic with a singly-bridged annulene (9) in which one ring contains (m+1) atoms, the other (n+1), and the perimeter (m+n). The bridges, however, involve out-of-phase overlap, indicated by the dashed lines in (9), so both small rings will be of antiHückel type (Ref.11).



(9)

For the perimeter ring to be aromatic, (m+n) must be of the form (4p+2). For the component rings to be aromatic, each must contain 4q atoms, since the rules for antiaromaticity are reversed for antiHückel systems (Ref.11). The rings can then all be aromatic if, and only if, m and n are each of the form (4r-1), i.e. 3,7,11,etc.. Otherwise at least one of the rings will be antiaromatic, in which case the overall stabilization is unlikely to allow the spirarene to exist as such. Furthermore, the aromatic energy of annulenes decreases with increasing ring size and the ease of internal combination to form a tricyclic species (e.g.(7)→(8)) will become greater, the larger m and n. It therefore seems clear that the only compound of this type that might conceivably exist as a stable species is [3,3] spirarene (8). However, in view of the poor overlap involved in the spiroconjugative interactions, it seems very unlikely that it will be isolable except in isolated form, e.g. in matrices at low temperatures.

We still have to consider the case of [m,n] spirarenes where m is even and n odd. Species of this kind can exist as ions or radicals. The latter will certainly be unstable to dimerization but stabilization of the ions may lead to significant chemical effect. These species can be treated in the same way as the [odd, odd] spirarenes. The perimeter is of odd cyclic Hückel-type with (m+n) atoms while the bridges each divide it into two even anti-Hückel systems with (m+1) and (n+1) atoms. It is easily seen that the rings can all be aromatic in the case of cations if m=4p and n=4q-1. Since spiroaromatic effects must decrease rapidly with ring size, the only system likely to be of interest is that with m=4 and n=3, i.e. the [4,3] spirooctatrienyl cation (10). In the anions series, the rings can all be aromatic only if m=4n-2 and n=4n-1. The only accessible system small enough for spiroaromatic interactions to be significant is then [3,2] spirohexadienyl anion (11).



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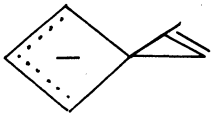
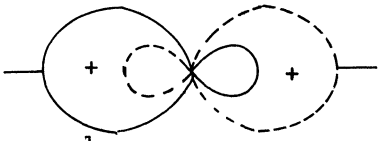


(11)

SIGMACONJUGATION

A long known fact whose consequences have nevertheless been largely overlooked is that even if two different sp^n hybrid AOs are orthogonal to one another, nevertheless the resonance integral between them does not vanish. This can be seen most clearly in the case of two sp hybrid AOs, ψ_1 and ψ_2, of an atom, given in terms of its s AO (s) an appropriate p AO (p) by $2^{-\frac{1}{2}}(s \pm p)$



$\psi_1 = \frac{1}{\sqrt{2}}(s-p)$ $\psi_1 = \frac{1}{\sqrt{2}}(s+p)$

The resonance integral (β) between ψ_1 and ψ_2, is given by

$$\beta = \int\psi_1 H\psi_2 d\tau = \frac{1}{2}\frac{1}{2}\int(s+p)H(s-p)d\tau$$

$$= \frac{1}{2}\frac{1}{2}\left\{\int\int sHsd\tau + \int sHpd\tau + \int pHsd\tau + \int pHpd\tau\right\} \quad (1)$$

The resonance integrals between s,p,d, etc. AOs do vanish, through symmetry, so the second and third terms in equation (1) are equal to zero, while the first and third are equal to the orbital energies of the AOs s(Es) and p(Ep) respectively. Hence

$$\beta = \frac{1}{2}(Es - Ep) \quad (2)$$

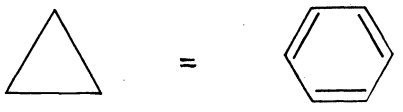
This does not vanish because Es is numerically greater than Ep. Indeed, in the case of carbon, Es - Ep is ~ 10eV (Ref.14) giving a value of 5eV (~100 kcal/mole) for β. Hardly negligible! The corresponding values for sp^2 and sp^3 carbon are given by expressions similar to equation (2) but with factors of 1/3 and 1/4, respectively. This even in the case of two sp^3 hybrid AOs of a carbon atom, β is almost double the value commonly attributed to the $2p\pi:2p\pi$ integral in a conjugated hydrocarbon.

The apparent localization of bonds in unconjugated compounds, in particular paraffins, is commonly attributed to the lack of interaction between adjacent CH bonds formed by sp^3 hybrid AOs, the argument being that there is no resonance interaction between the latter. Our argument shows this assumption to be not merely incorrect but wildly incorrect. How then can we explain the unquestionable fact, that bonds in such compounds do seem to be localized, in that molecular properties such as the heat of formation and dipole moment can be expressed as additive sums of corresponding bond properties and that the lengths of bonds of a given type in different molecules are the same? It should be noted that our estimate of the interactions is no figment of the imagination. Indeed, it has been obvious for some time that they must be large, from data provided by ultraviolet photoelectron spectroscopy (ups). If there were no interaction between the CH bonds in methane, its first ionization potential would be a superposition of four corresponding degenerate ionizations. In fact two bonds appear in the spectrum, one, triply degenerate and split by John-Teller effects, at 14 eV, the other at 22.5 eV. This pattern would be expected if the CH bonds do interact with one another and the splitting should amount to four times the effective β for the interaction. Thus β ~ 2 eV.

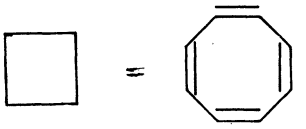
If the interactions between "localized" bonds are indeed large, the observed behaviour can be explained only if the interactions, while large, depend only on the bonds interacting, not on the rest of the molecule. If this is the case, we will be able to absorb their effects into the additive contributions we attribute to the various bonds, i.e. bond energies, bond moments, etc. This situation has indeed been shown to hold, both by PMO theory (Refs. 10-12 and by π SCF calculations (Ref.15) for classical polyenes which again exhibit "bond localization". A similar explanation for "localization" in the paraffins was given twenty-five years ago by Dewar and Pettit (Ref. 16), also in terms of PMO theory, on the assumption that the major interactions are between adjacent (1,2) bonds, due to interactions of the type under consideration here. (Ref.17).

To the approximation of second order perturbation theory, the interactions should depend only on the bonds involved. Writing the C-C-C, C-C-H, and H-C-H interactions as a, b, and c respectively, it can be shown that the interaction energy per CH_2 group in a n-paraffin has a constant value (a+4b+c). This accounts for the linear change in heat of formation with chain length. The only exception is in the first step, $CH_4 \rightarrow C_2H_6$. Here the methylene increment is predicted to differ from the standard one by -(a-2b+c). The overall interaction energy of a branched paraffin is predicted to differ from that of a linear one by the same amount in the opposite direction, i.e. +(a-2b+c), per branch while a double branch is predicted to be equivalent to <u>three</u> single branches. The available thermochemical data fit these predictions reasonably well, in, of course, the absence of steric effects, with (a-2b+c) ~-2 kcal/mole. The PMO treatment thus accounts quite satisfactory for the existence of apparent bond localization in polyenes, and for the observed deviations from additivity, even though the individual sp^3 hybrid carbon AOs interact strongly with one another.

The CC bonds in a paraffin thus form a σ-conjugated system, isoconjugate with the π system in a conjugated polyene. Each carbon atom in the paraffin plays the same role as a (=CH-CH=) unit in the polyene. In both cases, the β for interunit interactions (i.e. across a C-C bond in the paraffin or C=C in the polyene) are greater than the intraunit ones (between two adjacent CC bonds or across a polyene single bond). A cycloparaffin should therefore be isoconjugate with a cyclic polyene and hence liable to exhibit σ-aromaticity or σ-antiaromaticity; e.g.:



(12) aromatic (13)
number of CH_2 or C_2H_2 units odd



antiaromatic
number of CH_2 or C_2H_2 units even

The idea that cyclopropane (12) is an aromatic compound, while startling, does in fact account for much otherwise puzzling behaviour. In the first place, cyclopropane is unreasonably stable. Its strain energy (27 kcal/mole) is almost the same as that in cyclobutane (26 kcal/mole) although the angle strain at each vertex (51°) in cyclopropane is more than double that (21°) in cyclobutane (13). If the bending is harmonic, the total strain energy in cyclopropane, per CH_2 group, should then be $(51/21)^2 = 6$ times that in cyclobutane. Six times the value in cyclobutane (6.5 kcal/mole) amounts to 39 kcal/mole, more than four times the observed value of 9 kcal/mole. Inclusion of angle strain reduces the discrepancy but does not remove it. Allowing 3 kcal/mole for each eclipsing interaction, the strain per CH_2 in cyclobutane falls to 3.5 kcal/mole and that estimated for cyclopropane to 21 kcal/mole. It should moreover be noted that this is likely to be an underestimate because of anharmonicity in the bending mode which should make large angle compressions more expensive in energy than a parabolic potential would predict.

These results can be understood immediately if cyclopropane is in fact aromatic and cyclobutane antiaromatic. The apparent "strain energy" of cyclopropane will be less than the real value by the aromatic energy of cyclopropane while in cyclobutane, the observed "strain energy" is a sum of the real strain energy and the antiaromatic energy. It must, however, be remembered that cycloparaffins resemble cyclic polyenes with "classical"bond alternation. The effects of aromaticity and antiaromaticity should consequently decrease rapidly with increasing ring size (Ref.11) and are likely to be small even in the case of cyclobutane. In the higher cycloparaffins, no significant effects are likely as regards their total energies or other collective properties.

A second striking feature of cyclopropane is the fact that it undergoes chemical reactions which are qualitatively different from those of other cycloparaffins. It undergoes ring opening easily by electrophilic attack, it exhibits conjugative interactions with adjacent unsaturated groups, and the ring is also formed by internal cyclization processes with remarkable ease.

Thirdly, the geometry of cyclopropane is unexpected, the "weak" CC bonds being shorter (1.51Å) than those in n-paraffins or cyclohexane (1.53Å). Note that the bonds in cyclobutane are longer (1.55Å) than normal. The shortening is not a mere "banana bond" effect.

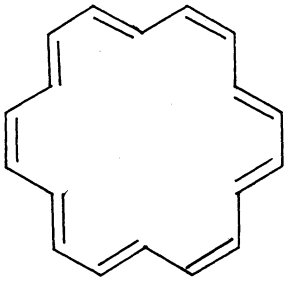
Finally, the idiosyncracies of cyclopropane have led to the open recognition that its behaviour cannot be satisfactorily interpreted in terms of its classical structure. In order to understand its properties, one has to use a MO ("Walsh orbitals") description. The parallel with benzene could hardly be closer!

These ideas can be extended to other microcyclic systems and again help to account for various features of their chemistry. For example, the strain energy of cyclopropane (52 kcal/mole) is surprisingly high, nearly double that of cyclopropane, given that the angle strain in it is only 8° more at each apex than in cyclopropane. The ratio between the real strain energies will, however, be much less than this because the sigmaaromatic stabilization of cyclopropane will be no greater than that of cyclopropane - and probably less in view of its lesser symmetry. Note that the strain energies of cyclobutene are identical. Many other examples could be cited.

WHY ARE LARGE CYCLIC POLYENES AROMATIC?

Some years ago we developed a semiempirical π SCF treatment (Ref.15) based on the Pople π approximation (Ref.18), which gave extraordinarily good predictions of molecular geometries and heats of formation for a very wide range of conjugated hydrocarbons, both aromatic and nonaromatic. Indeed, this remains by far the best treatment yet devised for calculating heats of formation of such species, the accuracy being comparable with that given by even good modern thermochemical measurements (except in cases where ring strain or steric effects intervene since no allowance was made for them). The only competing procedures are two very similar ones, one developed here (Ref.19) and the other by Lo and Whitehead (Ref.20). While π treatments are now out of fashion and of course limited in scope, the potential of these methods should be kept in mind.

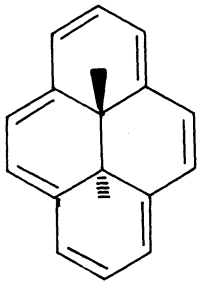
One of the compounds we studied was [18]annulene (14), (Ref.21) whose structure was then a subject of controversy. An X-ray structure determination (Ref.22) had been claimed to indicate an aromatic structure, with almost equal bond lengths and D_{6h} symmetry.



(14)

This conclusion seemed to be supported by its n.m.r. spectrum which indicated a diamagnetic ring current (Ref.23). On the other hand, its electronic spectrum seemed to indicate bond alternation (Ref.24), a conclusion later supported by molecular mechanics calculations (Ref.25). We were therefore interested but not unduly surprised to find that our treatment also predicted it to have alternating bonds with lengths (1.36, 1.46 Å) similar to those in classical polyenes.

Later, however, we found, much to our surprise, that our treatment also predicted bond alternation in [14]annulene and [10]annulene, a conclusion which was certainly incorrect in view of the properties of Boekelheide's dimethyldihydropyrene (15) (Ref. 26) and Vogel's methano[10]annulene (16). (Ref.27). Moreover Heilbronner (Ref. 28) on re-examining the spectrum of (13), found a strong bond in the infrared, ca 950 mμ, which had been previously overlooked. This invalidated the arguments (Ref.24) for bond alternation, based on the electronic spectrum. The crystallographic evidence could moreover have been discounted only if the crystals had consisted of random mixtures of the two Kekulé forms of (14), in which case the observed x-ray reflections should have shown distortions analogous to those due to large thermal motions. It was, however, specifically stated that no such effects were observed (Ref.22).



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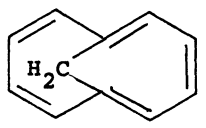

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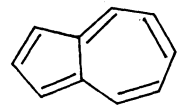

(17)

Thus it seemed clear that our treatment was underestimating the stabilization due to cyclic delocalization in the higher annulenes, even though it gave such good results for equally large molecules provided that these were built up from conjugated rings containing no more than seven atoms. Even azulene was calculated to be aromatic, although PMO theory shows this to contain a π system corresponding to a weakly perturbed [10] annulene.

We thought at the time that this failure might be due to the treatment of σ bonds in our π approximation, where we had assumed that their contributions could be represented in the same way as those of pure σ (i.e. single) bonds; i.e. as sums of bond energies and compressions energies, the latter estimated using Morse potential functions. However we later found that MINDO/3 led to similar errors, also predicting [18]annulene, (Ref. 21), and the bridged [10] and [14]annulenes (15) and (16) (Ref.29), to have alternating CC lengths (1.36 and 1.46A). Moreover the heat of formation estimated for [18] annulene (129.3 kcal/mole) and the difference in energy between the D_{3h} and D_{6h} structures (25.7 kcal/mole) were quite close to the values given by the π approximation, (Ref.30), i.e. 116.8 and 28.8 kcal/mole, respectively. Both heats of formation also agree with a recent experimental value (124.0 kcal/mole (Ref. 31)).

MINDO/3 does, however, perform relatively poorly in the case of aromatic compounds, giving heats of formation for benzene and naphthalene that are too positive by 9.0 and 21.2 kcal/mole respectively. Since this error had apparently been corrected in MNDO (Ref.6), we decided to apply this procedure to the annulene problem.

As figure 1 shows MNDO does indeed give very good estimates for the heats of formation of several benzenoid hydrocarbons and also satisfactory values for the lengths of the bonds in them. However, like MINDO/3, it predicted alternating bond lengths in azulene (17), [18]annulene (14), and Boeckelheide's [14]annulene (15) while the bridged [10]annulene (16) was predicted not to exist as such, collapsing to the tricyclic isomer (18). The heat of formation calculated for [18]annulene (141.9 kcal/mole) was a good deal higher than that given by the two other methods. While the difference in energy between the D_{3h} and D_{4h} structures was somewhat less (21.5 kcal/mole).

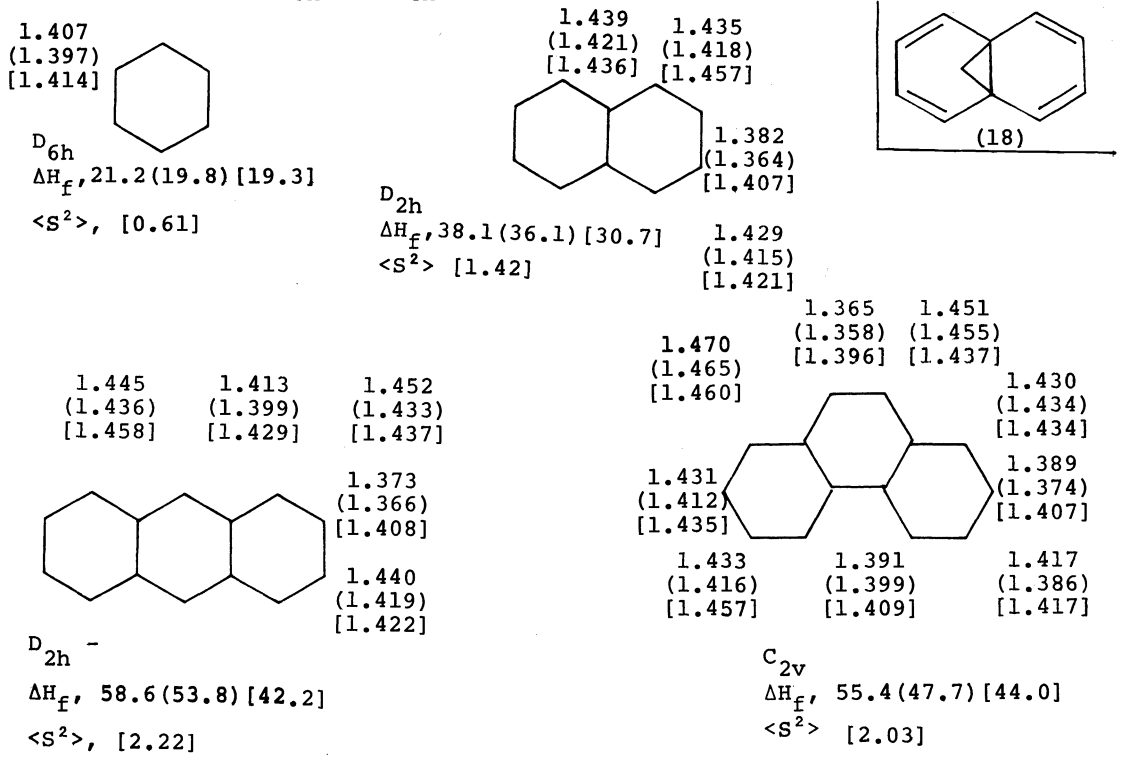

Figure 1. Symmetries, bond lengths (Å), heats of formation (ΔH_f; kcal/mole), and unpaired spin ($\langle s^2 \rangle$) in benzenoid hydrocarbons, given by MNDO (experiment)[UMNDO].

It would of course be nice to have calculations by other procedures for comparison. Unfortunately the molecules in question are too large to be treated by any method as trustworthy as those we have already used. It should again be emphasized that calculations in connections such as this are worthless unless carried out with complete geometry optimization. Even the most innocuous-seeming assumptions, e.g. lengths or angles of bonds to hydrogen, can easily lead to errors of 10-20 kcal/mole when summed over a molecule of the size of those we are considering. The use of geometries calculated by other methods or taken from experiment, is even more objectionable.

However, as we have pointed out, the failure of any one of the three methods we have used is surprising, given their success in other connections. Furthermore, as we have also already noted, a study of [18]annulene by molecular mechanics (Ref.25) also led to the incorrect prediction of bond alternation, with a considerable difference (10 kcal/mole) between the D_{3h} and D_{6h} structures. We therefore felt convinced that some factor must be operating in the case of the higher annulenes which encourages delocalization and which is not taken into account in the orbital (Hartree-Fock) approximation.

An intriguing possible candidate seemed to be electron-pair correlation between the pairs of electrons occupying π MOs. Not only are the conjugated systems in annulenes alternant (Ref. 1,2) but they contain equal numbers of single and double bonds in each Kekulé structure. The electrons occupying a given MO could reduce their mutual repulsion if one of them spent more time in the "single" bonds and the other in "double" ones. This type of correlation can become important only if the electron populations of both kinds of bonds are similar, i.e. if they have similar bond orders and are equally strong. Such a correlation effect should tend to promote delocalization in cyclic conjugated systems, exactly the property we are looking for. Furthermore, it will of course be neglected in any SCF MO treatment since neglect of coulombic electron correlation is the basis of the Hartree-Fock approximation.

The type of correlation we are considering leads, in MO terminology, to a situation where two electrons, which would normally be occupying a single joint MO, now occupy two different MOs, with different orbital densities in the two sets of bonds. Furthermore, spin correlation will favor a situation where the electron pairs in different orbitals are also correlated, the α-spin electrons being concentrated in one set of bonds while the β-spin ones are in the other. This picture corresponds to the Pople-Nesbet spin-unrestricted Hartree-Fock (UHF) approximation (Ref.32) where electrons with different spins occupy different sets of orbitals. This procedure is commonly used in calculations for open shell systems (radicals, triplets, etc.) where the uncoupling of the electron pairs is due to the presence of unpaired electrons in singly occupied orbitals. It has been very little used for closed shell systems, presumably because there seems no obvious reason why the electrons in them should be unpaired. Other expedients have therefore been used to allow for electron correlation in such cases. Use of the UHF version of MNDO (UMNDO) in the case of small, "normal", closed shell molecules does indeed lead as a rule to identical sets of MOs for both sets of electrons. Most of the exceptions encountered up till now have been molecules with significant biradical character, where two electrons tend to segregate themselves in different regions even though their spins are antiparallel. This can occur if the HOMO and LUMO are degenerate, or nearly degenerate, so that the repulsion between the two electrons can be reduced if they occupy different orbitals and if the difference in energy between the orbitals is small enough for the corresponding excitation energy to be outweighed by the reduction in electron repulsion. According to our present suggestion, a similar situation may hold in the case of molecules which have no biradical character in this sense but in which the valence electrons are sufficiently delocalized for segregation to be energetically profitable. This may occur not only in aromatic systems of all kinds but also in linear ones, for example ions such as allyl $(CH\cdots CH\cdots CH_2)^{\pm}$ or pentadienyl $(CH_2\cdots CH\cdots CH\cdots CH\cdots CH_2)^{\pm}$. The effect should be particularly marked in the higher annulenes where more bonds are involved and where each classical (Kekulé) structure contains equal numbers of single and double bonds.

As figure 1 shows, the results for benzene and naphthalene given by UMNDO were almost the same as the MNDO ones and the differences in the case of anthracene and phenanthrene were not large. Dramatic changes took place in the case of the other molecules, however, as can be seen from figure 2.

All these molecules are now predicted to have symmetrical "aromatic" structures with bond lengths close to the value in benzene. The heats of formation calculated by UMNDO are also much less positive than those from MNDO. Results are also included for a second derivative of [14]annulene and for cyclobutadiene, the latter being a typical "biradical" in its square form. While MNDO predicts the singlet ground state of cyclobutadiene to be rectangular, UMNDO predicts it to be square, with D_{4h} symmetry. Figure 2 also shows the bond lengths for [18]annulene given by the x-ray crystallographic studies (Ref.22). The agreement with the UMNDO values is qualitatively correct, predicting the correct (D_{6h}) symmetry and the relative lengths of the two types of CC bond. The difference between the two bond lengths is, however, underestimated, indicating that UMNDO overestimates the efficiency of delocalization in (14). Note also that (16) is predicted to have the observed bicyclic structure, not the tricyclic one (18) given by MNDO.

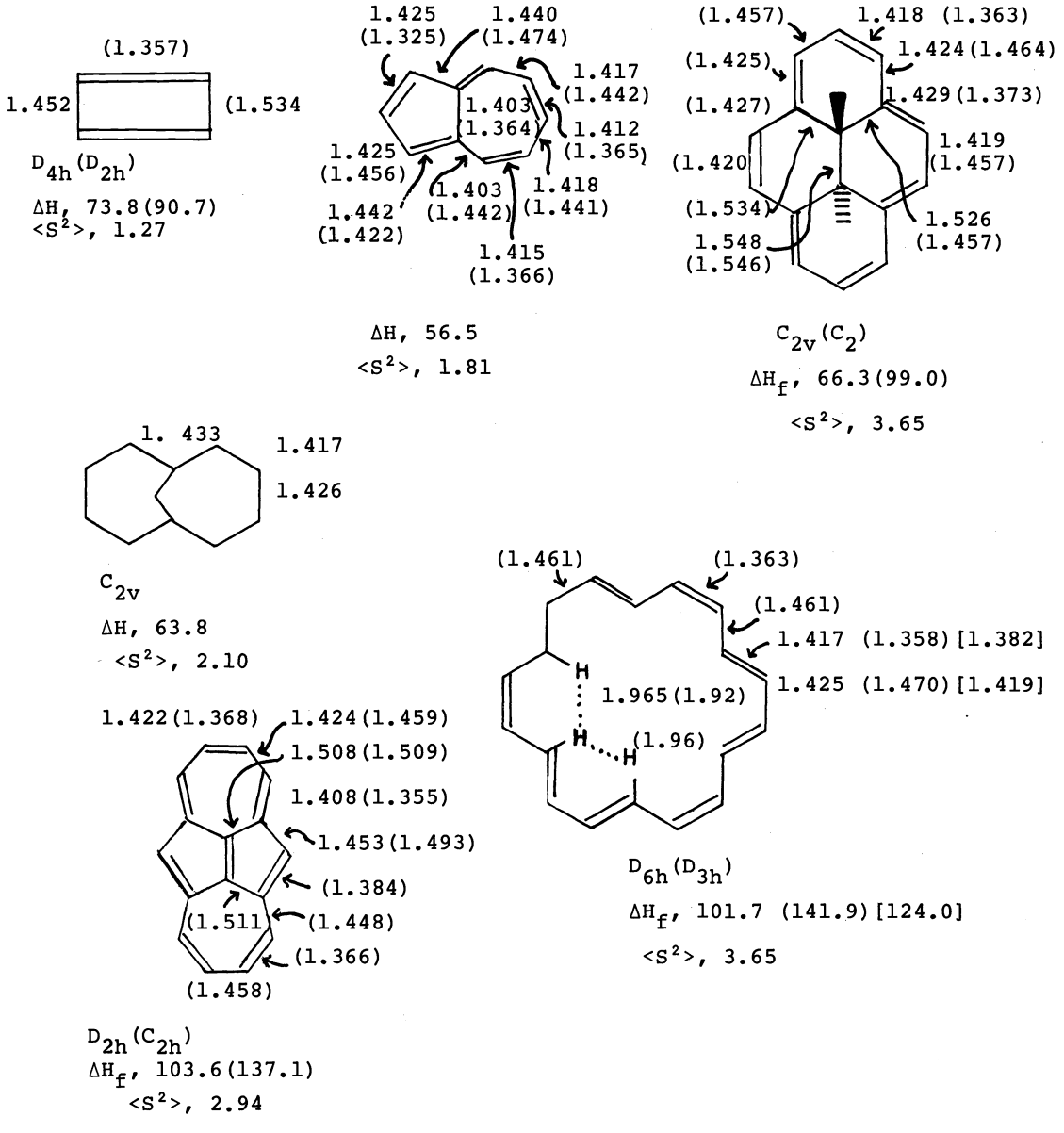

Figure 2. Symmetries, bond lengths (Å), heats of formation (ΔH_f; kcal/mole), and unpaired spin ($\langle S^2 \rangle$) for annulene derivatives, calculated by UMNDO (MNDO). Experimental values are given in square brackets ([]).

The extent to which the electrons are unpaired in the UMNDO treatment can be quantified by summing the total (scalar) unpaired spins on the various atoms. This is the quantity denoted by $\langle S^2 \rangle$ in figure 1 and 2. It will be seen that $\langle S^2 \rangle$ is small for benzene and naphthalene but becomes large for the larger annulenes. It will also be seen that the average value of $\langle S^2 \rangle$ per conjugated carbon atom is less than 0.15 for the "normal" aromatic compounds but greater than 0.2 for the annulenes. Azulene (0.18) occupies a border position. Our intuition that spin unpairing is the factor that stabilizes aromatic structures in the higher polyenes therefore seems to have been correct. There are, however, two discrepancies to be cleared up; the fact that the UMNDO heats of formation are too negative, by 22 kcal/mole in the case of [18]annulene, and the incorrect prediction that singlet cyclobutadiene is square (Ref.33).

UMNDO is known to give heats of formation that are too negative in the case of open shell compounds. The reason for this is that it allows too completely for correlation, in particular in the case of biradicals and triplet states. Since allowance is made in MNDO for electron correlation, viz the parametrization, and since UMNDO uses the same parameters, the correlation energy for the two "unpaired" electrons in a biradical or triplet is calculated twice over, leading to total energies which are too negative. In the case of "genuine" biradicals, where the unpaired electrons effectively occupy orbitals widely separated in space, the error should amount to the mean electron pair correlation energy in molecules, i.e. 1 eV. The UMNDO heats of formation for such species are systematically too negative by 20-25 kcal/mole. This error is less if the "singly occupied" orbitals are MOs derived from AOs of the same set of atoms because now the contribution to the total correlation energy of the "unpaired" electrons due to segregation of the electrons in different MOs, is only part of the whole. Lack of data have prevented us from establishing a quantitative relationship. We have been forced to assume that the best value for the heat of formation will be given by the more negative of two estimates, one the MNDO value, and the other the UMNDO value plus 20 kcal/mole. It will be seen from Table 2 that according to this rule, the MNDO value for cyclobutadiene should be accepted, the lowering given by UMNDO being an artifact. Equally, the bonds in it should alternate as MNDO predicts and as in fact they do (Ref.33).

The situation in the other annulenes is more complicated because here several pairs of electrons are uncoupled. Since both electrons in each case occupy π MOs constructed from AOs of the same set of atoms, the correction to the UMNDO heats of formation should be less than for "genuine" biradicals. The correction should usually be proportional to the extent of unpairing, which can be equated to the quantity $\langle S^2 \rangle$. However, for compounds where the differences between the MNDO and UMNDO heats of formation are small, the correction is likely to be less because the UMNDO structures are then stabilized by spurious changes in geometry due to the overestimation of resonance stabilization. Indeed, one can get a good estimate of the heats of formation for the compounds in Tables 1 and 2 for which thermochemical data are available by taking the more negative of two quantities, one the heat of formation predicted by MNDO and the other (ΔH_f^{corr}) calculated from the UMNDO heat of formation (ΔH_f^{U}) by

$$\Delta H_f^{corr} = \Delta H_f^{U} + 5\langle S^2 \rangle$$

It should be noted in conclusion that our approach bears an obvious resemblance to Löwdin's alternant orbital method (Ref.34) which was also based on the special properties of alternant systems. Löwdin, however, considered segregation of electrons between different sets of atoms (starred and unstarred), not bonds, using an assumed relation between the relative values of the two sets of coefficients. It should also be noted that Baumann (Ref. 35) has recently shown that inclusion of configuration interaction in a CNDO-derived treatment of the higher annulenes leads to symmetrical structures, in particular for [18]annulene, whereas the corresponding single-configuration treatment gave bond alternation, like MINDO/3 or MNDO. This approach naturally throws no light on the reasons why electron correlation stabilizes higher annulenes in their symmetrical forms and the results were also made uncertain by failure to optimize geometries. Indeed, optimization of geometries presents problems in any method based on the use of CI. One major advantage of UMNDO is that it leads to variationally optimized wave functions and that derivatives of the energy can be calculated very easily. This enables geometries to be calculated without difficulty, using standard gradient optimization methods. All the geometries reported here were

optimized completely without making any assumptions. The procedures used have been described in detail elsewhere (Ref.6).

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