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Theoretical study of the in-plane components of the ^{13}C shielding tensors in condensed aromatic hydrocarbons

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The Pople model for chemical shielding is applied to calculate the in-plane components of the ^{13}C shielding tensors of condensed aromatic hydrocarbons. The wave functions are evaluated using the MNDO method and the calculated results are supported by the very good agreement with the experimental results in the few cases in which experimental information is available.

The relationship found between the calculated bond orders and the in-plane components of the ^{13}C shielding tensors suggest that the experimental study of the ^{13}C shielding tensors in these compounds may provide a powerful technique for studying aromaticity. The in-plane components are found to be directly affected by the degree of delocalization of the π-electrons in the adjacent bonds. Rules are given for estimating the orientation of the two in-plane components of the shielding tensor.

Key words: Shielding tensors — MNDO — Bond orders — Aromaticity

1. Introduction

The study of condensed aromatic hydrocarbons have attracted a great deal of attention from both theoretical and experimental workers [1-3]. The theoretical interest in condensed aromatic hydrocarbons is centered in the nature of their aromatic character (i.e. the degree of delocalization of the π-electrons), as manifest in structural and reactive properties of the molecules. Most of the theoretical studies have been directed towards molecular properties such as energy, UV spectra, etc. and their relationship to Kekulé resonance structures [4-7]. These studies addresss the problem of aromaticity of the molecule as a whole but fail to indicate the difference in localization of the π-electrons either in smaller molecular moieties or in individual bonds.

The liquid ^{13}C NMR of many of these compounds have been known for a number of years [8, 9], but only recently the complete ^{13}C shielding tensors in a fused aromatic ring compound such as pyrene have been measured [10]. The shielding tensors of fused aromatic hydrocarbons are characterized by two components, σ_{11} and σ_{22}, at lower fields which lie in the molecular plane. These two components are the subject of this study. The other shielding component, σ_{33}, is found upfield close to TMS, and is oriented perpendicular to the molecular plane. It is well established that the aliphatic character of σ_{33} originates in its relative independence of the π-electron structure responsible for the large down-field shift of the two in-plane components. The recent success of the MNDO semiempirical wave functions to correlate the experimental values of the two in-plane shielding components for all carbons in pyrene provides the impetus for this work. A variety of condensed aromatic hydrocarbons were selected to illustrate the high sensitivity of σ_{11} and σ_{22} on details of π-electron delocalization. The semiempirical wave function and/or the approximations used here are inadequate to correlate the σ_{33} data which depends primarily on the σ-electron structure.

The analysis of the results provides relationships between the calculated in-plane components of the ^{13}C chemical shielding tensors and the degree of delocalization of the π-electrons as measured by the MNDO [11] calculated bond orders.

2. Calculations

The limitations of current computational capabilities preclude the application of *ab initio* methods to molecular systems as large as those considered in this paper, but it has been exhibited that semiempirical approaches can be used successfully to reproduce experimental trends within a series of related compounds [12]. Further, it is known that the diamagnetic contribution to the ^{13}C shielding tensor is relatively constant between different molecules and therefore does not contribute significantly to the relative chemical shift nor to the large anisotropy of aromatic shielding tensors [12]. Consequently only the paramagnetic contributions will be considered in the following semiempirical model.

Using the well established Pople model for the isotropic chemical shielding [13, 14] the paramagnetic contribution to the shielding of the A nucleus is given by:

$$\begin{aligned}\sigma_{\alpha\beta}^{(p)} = -K \sum_{j}^{\text{occ}} \sum_{k}^{\text{unocc}} ({}^{1}E_j^k - {}^{1}E_0)^{-1} \\ \times \sum_{\mu<\nu}^{\text{A}} \sum_{\lambda<\sigma}^{\text{B}} (C_{\mu j}C_{\nu k} - C_{\nu j}C_{\mu k})(C_{\lambda j}C_{\sigma k} - C_{\sigma j}C_{\lambda k}) \\ \times \langle \phi_\mu | r^{-3} L_\alpha | \phi_\nu \rangle \langle \phi_\lambda | L_\beta | \phi_\sigma \rangle,\end{aligned} \tag{1}$$

with

$$K=\frac{\mu_0 e^2 h^2}{2\pi m^2},$$

and the usual notation is used [12]. In this approach, if only *s* and *p* orbitals are used in the basis set, only local terms are included in the calculation, the ΔE approximation is taken, and the closure relationship for a ZDO (Zero Differential Overlap) [15] wave function is used:

$$\sum_j^{\text{occ}} C_{\mu j}C_{\lambda j}+\sum_k^{\text{unocc}} C_{\mu k}C_{\lambda k}=\delta_{\mu\lambda}. \tag{2}$$

The tensor shielding components for the nuclei A are then given by:

$$\sigma_{xx}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle\left[P_{y_\mathrm{A}y_\mathrm{A}}+P_{z_\mathrm{A}z_\mathrm{A}}+\sum_\mathrm{B}(P_{y_\mathrm{A}z_\mathrm{B}}P_{y_\mathrm{B}z_\mathrm{A}}-P_{y_\mathrm{A}y_\mathrm{B}}P_{z_\mathrm{A}z_\mathrm{B}})\right] \tag{3a}$$

$$\sigma_{yy}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle[P_{x_\mathrm{A}x_\mathrm{A}}+P_{z_\mathrm{A}z_\mathrm{A}}+\sum_\mathrm{B}(P_{x_\mathrm{A}z_\mathrm{B}}P_{x_\mathrm{B}z_\mathrm{A}}-P_{x_\mathrm{A}x_\mathrm{B}}P_{z_\mathrm{A}z_\mathrm{B}})] \tag{3b}$$

$$\sigma_{zz}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle[P_{x_\mathrm{A}x_\mathrm{A}}+P_{y_\mathrm{A}y_\mathrm{A}}+\sum_\mathrm{B}(P_{x_\mathrm{A}y_\mathrm{B}}P_{x_\mathrm{B}y_\mathrm{A}}-P_{x_\mathrm{A}x_\mathrm{B}}P_{y_\mathrm{A}y_\mathrm{B}})] \tag{3c}$$

$$\sigma_{xy}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle\sum_\mathrm{B}(P_{z_\mathrm{A}z_\mathrm{B}}P_{y_\mathrm{A}x_\mathrm{B}}-P_{z_\mathrm{A}x_\mathrm{B}}P_{y_\mathrm{A}z_\mathrm{B}}) \tag{3d}$$

$$\sigma_{xz}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle\sum_\mathrm{B}(P_{y_\mathrm{A}y_\mathrm{B}}P_{z_\mathrm{A}x_\mathrm{B}}-P_{y_\mathrm{A}x_\mathrm{B}}P_{z_\mathrm{A}y_\mathrm{B}}) \tag{3e}$$

$$\sigma_{yz}^{\mathrm{A}}=\frac{-K}{\Delta E}\langle r^{-3}\rangle\sum_\mathrm{B}(P_{x_\mathrm{A}x_\mathrm{B}}P_{z_\mathrm{A}y_\mathrm{B}}-P_{x_\mathrm{A}y_\mathrm{B}}P_{z_\mathrm{A}x_\mathrm{B}}), \tag{3f}$$

where the elements of the electron density matrix are defined by [15]:

$$P_{\mu\nu}=\sum_j^{\text{occ}} C_{\mu j}C_{\nu j}. \tag{4}$$

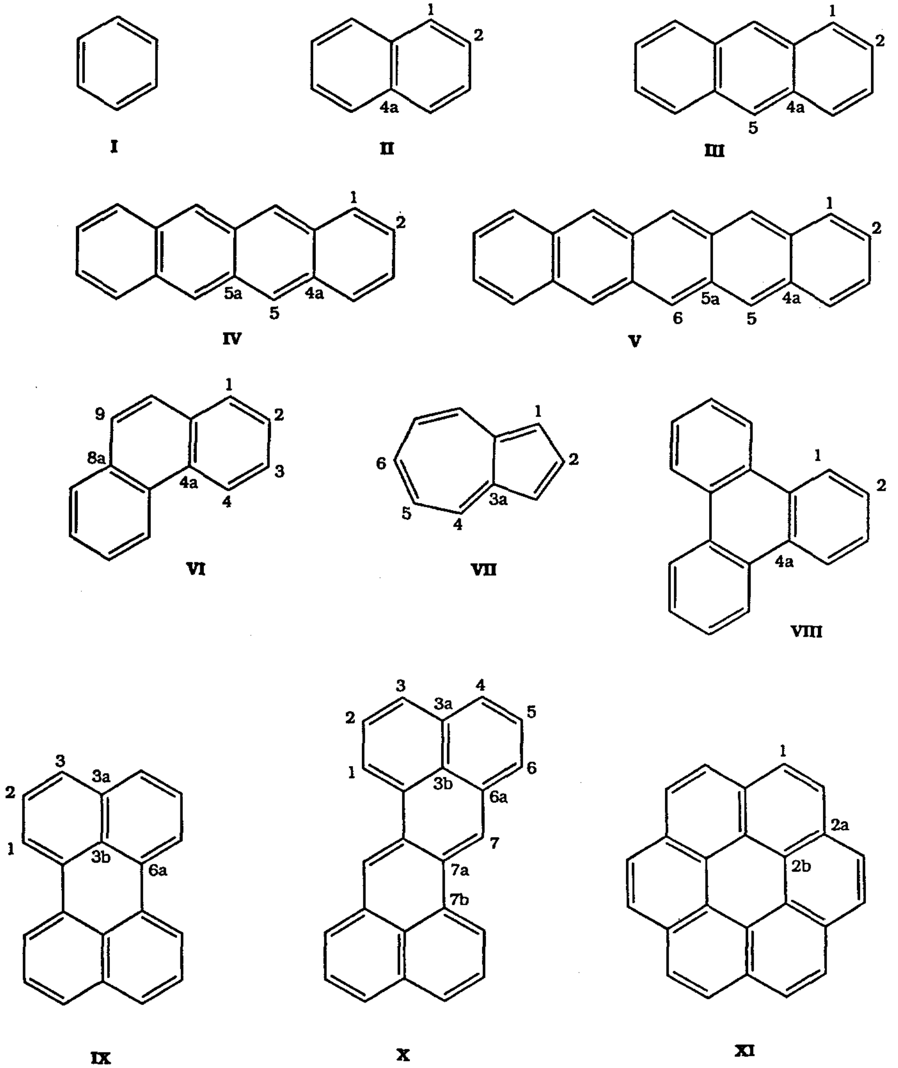
Taking into account that the TMS scale reverses the sign of the shielding scale, the components of the shielding tensors are related to the electronic density matrix by equations of the type:

$$\sigma_{\alpha\beta}^{(\mathrm{TMS})}=Af_{\alpha\beta}(P_{\mu\nu})+B, \tag{5}$$

where A and B are scaling parameters. A is a fitting number which includes K and the molecular parameters $\langle r^{-3}\rangle$ and ΔE. The $f_{\alpha\beta}(P_{\mu\nu})$ are given by Eqs. (3a–f) less the constants included in A. The value B references the chemical shift scale.

The success of the approximations used in Eqs. (3, 5) have been tested in pyrene with excellent results [10] providing a justification for the use of the model in other condensed aromatic hydrocarbons. It is clear that the actual calculated magnitudes of σ_{11} and σ_{22} depends on the empirical parameters A and B, but the relative trends and the calculated orientation of the shielding tensor principal components are independent of A and B. In this work the A and B parameters ($A = 151.17$ ppm, $B = -22.02$ ppm) obtained in pyrene [10] are used to scale the calculations. These parameters are used pending the availability of experimental information on other condensed aromatic compounds. Because these values may include rather drastic approximations for some of the fused aromatics studied here, the calculation of these in-plane shielding components with this simplified model is only intended to predict relative shift values and the relative spatial orientation of the principal axes.

It should be noted that the correlation of the calculated results with the isotropic



Scheme. Carbon numbering in the compounds studied in this paper chemical shifts is not possible because the calculated σ_{33} components, which lie perpendicular to the plane, are not adequately treated by the MNDO wave functions in this approximation [10]. The σ_{33} component, which has an aliphatic value, lies between -10 and 40 ppm on the TMS scale and is determined by the σ-electron structure of these molecules. As σ_{33} is independent of the π-electrons, this component does not provide significant information on the aromatic properties of the compound.

Except for azulene (VII),where the experimentally determined structure [16] was used, the calculations reported here were performed using idealized geometries based on the experimental distances in benzene [17]. A standard version of the MNDO program was used in the calculations.

3. Results and discussion

Figure 1 gives the MNDO [11] calculated bond orders. The bond orders between atoms A and B were calculated using the well known equation [15]

$$P_{AB} = \sum_{\substack{\mu \in A \\ \nu \in B}} P_{\mu\nu} \tag{6}$$

where the $P_{\mu\nu}$ are the elements of the density matrix defined by Eq. 4.

In Table 1 the calculated values of the in-plane shielding components are given and the calculated orientation of the principal shielding axes are presented in Fig. 2. In each instance the numbering system is provided by the Scheme.

a. Protonated carbons

The calculated values for the protonated carbons in Table 1 are quite similar to those calculated in benzene (I), $\sigma_{11} = 220\,(234)$ ppm and $\sigma_{22} = 146$ (146) ppm, (experimental values given in parenthesis [18]). Significant differences are observed for the protonated carbons in azulene (VII) and for σ_{22} in C_7 in zethrene (X). The variations observed in VII reflect both the unusual electronic structure and the different geometry of azulene. Particularly interesting is the downfield movement of σ_{22} and upfield movement of σ_{11} in both C_1 and C_2, the carbons in the five member ring. Furthermore, the values of σ_{22} in C_4, C_5 and C_6 are about 10 ppm downfield from those of benzene and the σ_{11} values are somewhat higher than in benzene for the protonated carbons in the seven member ring. All these effects may be associated with the change in geometry, but a systematic theoretical study of this dependence has been deferred until experimental data on the shielding tensors have been obtained.

The upfield shift of σ_{22} of C_7 in X reflects a shift which is more typical of ethylene [19] than benzene. Note from Fig. 1 that the C_7–C_{7a} bond in X is formally a double bond, making the orientation of the C_7 and C_{7_a} tensors more like those in ethylene than those in benzene (see Fig. 2).

Table 1. Calculated principal values of the in-plane components of the ^{13}C shielding tensors in condensed aromatic hydrocarbons[a]

Compound		σ_{22}	σ_{11}
Benzene (I)	C	146	220
Naphthalene (II)	C_1	142	219
	C_2	139	222
	C_{4a}	190	202
Anthracene (III)	C_1	142	219
	C_2	142	222
	C_5	145	214
	C_{4a}	188	203
Naphtacene (IV)	C_1	142	219
	C_2	141	222
	C_5	145	213
	C_{4a}	185	206
	C_{5a}	190	201
Pentacene (V)	C_1	141	219
	C_2	141	222
	C_5	144	213
	C_6	145	212
	C_{4a}	183	207
	C_{5a}	188	203
Phenanthrene (VI)	C_1	145	218
	C_2	144	221
	C_3	144	221
	C_4	145	219
	C_9	140	220
	C_{4a}	185	204
	C_{8a}	188	202
Azulene (VII)	C_1	160	202
	C_2	154	210
	C_4	133	219
	C_5	132	229
	C_6	135	224
	C_{3a}	159	219
Triphenylene (VIII)	C_1	144	220
	C_2	144	221
	C_{4a}	181	207
Perylene (IX)	C_1	142	219
	C_2	143	222
	C_3	144	218
	C_{3a}	195	197
	C_{3b}	192	198
	C_{6a}	174	211
Zethrene (X)	C_1	144	218
	C_2	143	222
	C_3	144	218
	C_4	144	217
	C_5	144	222

Table 1—continued

Compound		σ_{22}	σ_{11}
	C_6	143	217
	C_7	136	217
	C_{3a}	195	197
	C_{3b}	192	198
	C_{6a}	180	208
	C_{7a}	165	217
	C_{7b}	176	211
Coronene (XI)	C_1	143	219
	C_{2a}	191	199
	C_{2b}	188	200

[a] All values in ppm reference to TMS. Numbering according to the Scheme. The values were calculated using $A = 151.17$ ppm and $B = -22.02$ ppm. These values were obtained from a correlation with the experimental values measured in pyrene [10], therefore, the experimental principal values in the molecules calculated here may differ somewhat due to variations in ΔE. The lack of experimental values precludes further refinements in the A and B parameters for the time being

From the results in Fig. 2 it is clear that in all cases the axis associated with the downfield component lies close to the C–H bond in agreement with data on benzene [19]. In the absence of symmetry, the σ_{11} axis may deviate from the C–H bond by up to 20°. In most cases, however, this angle is under 10°. The deviation of the σ_{11} axis from the C–H direction in all cases can be rationalized in terms of the MNDO bond orders of the adjacent C–C bonds. The σ_{11} axis tends to orient along the direction which is perpendicular to the bond with the largest π-bond character or bond order. In C_7 of X, σ_{11} lies at 15° from the C–H bond and 105° from the formal double bond C_7–C_{7a}. While in ethylene σ_{11} lies perpendicular to the double bond [20]. In II, III, IV, and V it is observed that the deviations of σ_{11} from the C–H direction increases as one moves from the middle to the terminal ring. The corresponding differences between the calculated bond orders of the two adjacent C–C bonds also shows an increasing trend.

In phenanthrene (VI), the calculations of the two in-plane components at C_4 do not show any effect from the steric crowding of their associated protons. It is known that the upfield isotropic chemical shift of C_4 is anomalous [8], but the absence of any effect on the in-plane components it is not totally surprising because it has been established that a similar upfield steric shift of the $^{13}CH_3$ chemical shift in *cis*-butene, compared with *trans*-butene, originates entirely in the component perpendicular to the molecular plane [21]. Thus, it is the σ_{33} component C_4 in VI which is expected to account for most of the upfield isotropic shift.

The analysis of the results on the protonated carbons shows that the orientation of the in-plane shielding components is determined by the relative π-bond character of adjacent C–C bonds. Therefore, shielding tensorial data can provide a powerful tool in the study of aromaticity or of the degree of delocalization of

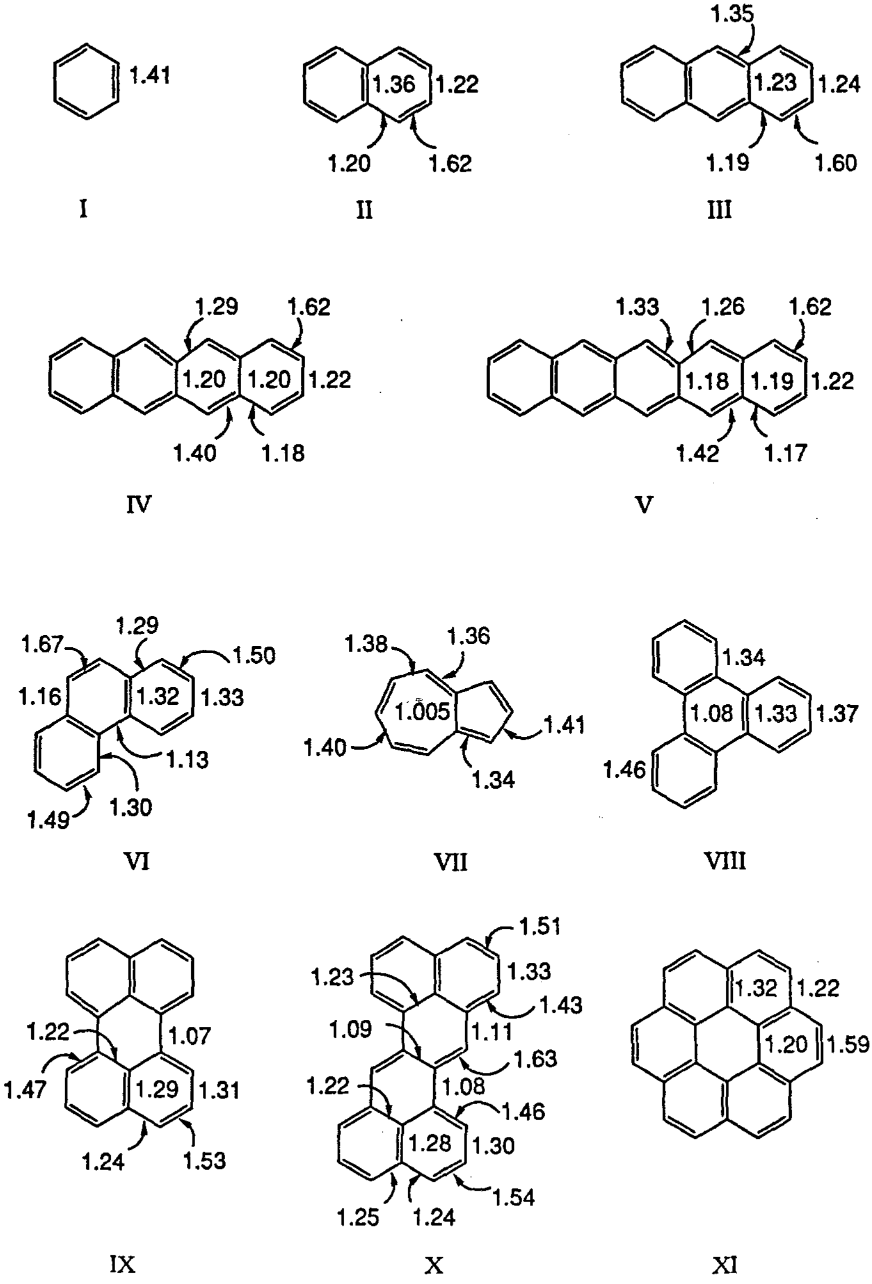
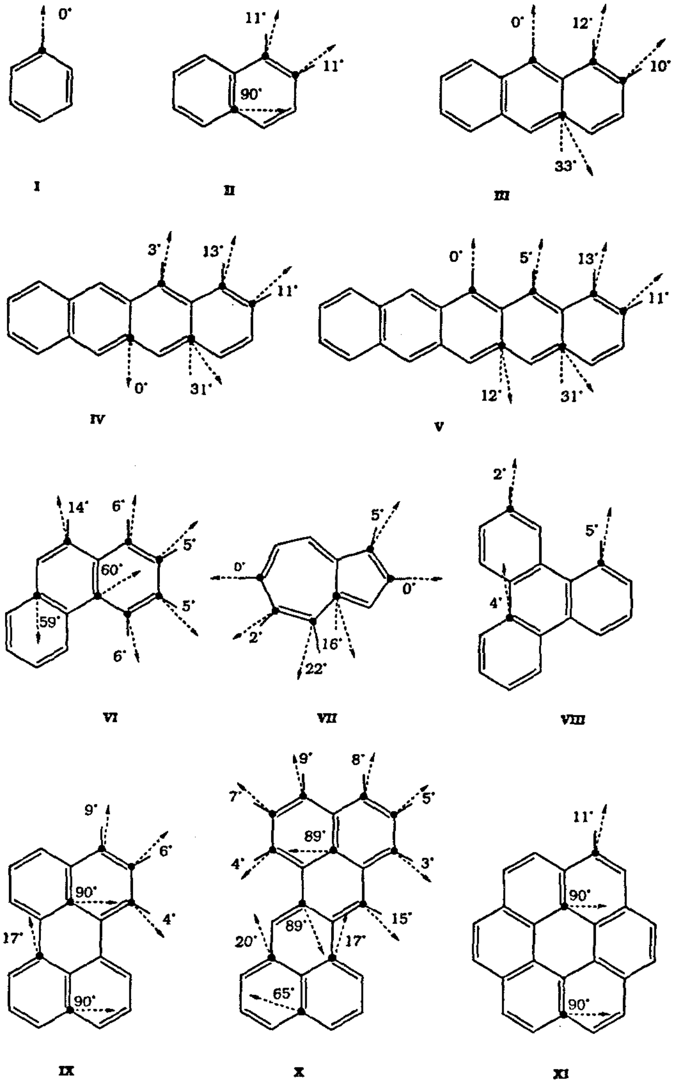


Fig. 1. MNDO calculated bond orders, given by Eq. 6, in the compounds studied in this paper



I II III

IV V

VI VII VIII

IX X XI

Fig. 2. Calculated orientation of σ_{11} ^{13}C shielding components in condensed aromatic hydrocarbons. σ_{22} is perpendicular to σ_{11} in the molecular plane

the π-electrons for various regions of an aromatic molecule. Unfortunately it is not yet possible to compare all of the calculated values with the corresponding experimental quantities but the excellent agreement found in pyrene [10] provides a basis for these analyses. It is important to note that even if the calculated principal values may exhibit large discrepancies relative to the corresponding experimental values due to variations in ΔE from one compound to another, the calculated orientations of the shielding tensor axes depend only on relative magnitudes. Thus, it is reasonable to expect that orientational information will be less affected by such variations in ΔE.

b. Bridgehead carbons

In the case of quaternary carbons no significant body of data yet exists upon which a precedent can be established for setting the orientations of the in-plane shielding components. Actually the only experimental data available to the authors knowledge are those for pyrene, which have been rationalized using the theoretical method described here [10]. For quaternary carbons there are two questions on the orientation of the in-plane components: (a) what are the features in the three adjacent C-C bond which govern the alignment of the σ_{11} component and (b) how great is the rotation of the axis associated with σ_{11} and in what direction does it rotate when all three bonds are not equivalent? If all three C-C bonds attached to a bridgehead carbon have the same bond orders, one may expect σ_{11} to equal σ_{22} barring inequivalence due to long range effects and an axially symmetric or near axially symmetric tensor should obtain. When only two of the three C-C bonds have equal bond orders (usually because of molecular symmetry) then σ_{11} lies along or perpendicular to the third C-C bond depending on whether the third bond has respectively a smaller or larger bond order in comparison with the two equal bond orders. When all three bonds have different bond orders, σ_{11} will tend to orient perpendicular to the bond of greatest π-bonding and along the bond with the smallest π-bonding and along the bond with the smallest π-bond order. The exact orientation depending upon the respective magnitudes of the three different bond orders. When all three bonds have comparable bond orders the two in-plane components of necessity must have similar values and the orientation of the two in-plane principal axes is more difficult to set, becoming degenerate in the axially symmetric limit. Near this limit, errors in the MNDO method may become sufficiently large as to make the orientational calculation very ill conditioned and unreliable. Note that the bridgehead carbons are similar to protonated carbons except that the C-H bond always exhibits the smallest bond order, and dominates the orientation of σ_{11} along the C-H bond. Methyl or alkyl substituted benzenes [19] respond much the same as in the protonated carbons as the C-R bond always has low π-bond character and σ_{11} will tend to orient along the C-R bond.

In Table 1 it is readily observed that the shielding tensors of bridgehead carbons in fused aromatic rings usually exhibit smaller anisotropies for the in-plane components than observed in the protonated carbons. This is not surprising as all three C-C bonds surrounding a bridgehead exhibit π-bond character and usually have comparable bond orders. In the quaternary carbons of compounds II, IV, and V it is observed that σ_{11} lies closer to the bridge bond in the center of the molecules, but the angular deviation from the bridge bond increases for the bridgehead carbons as one moves closer to the terminal rings. In II σ_{11} is oriented actually perpendicular to the bridge between the rings in accordance with the bond order for C_{4a}-C_{8a} being larger than the other two C-C bonds, making the orientation of σ_{11} in naphthalene (II) unique for this homologous series.

It is very interesting to observe the large anisotropy calculated for the shielding tensor of C_{3a} in VII, this quaternary carbon exhibits the largest anisotropy of those presented here. The relatively large difference between σ_{11}, which lies close to the C–C bridge and σ_{22} is comparable to that observed in protonated carbons. This large anisotropy can be rationalized in terms of the very low bond order in the bridge bond, which is practically a single bond. It is well known that there is no delocalization of the π-electrons in this bond in agreement with the observation that none of the Kekulé structures for azulene (VII) has a double bond across the bridge.

In perylene (IX) the shielding components of the $3a$ and $3b$ quaternary carbons show the same characteristics as those in II, indicating that IX exhibits the structure of two napthalene rings joined at C_1 and C_8. Once again it is the bond order between C_{3a} and C_{3b} which is largest and forces σ_{11} to be perpendicular to this bridge bond. Similar observations hold for the bridgehead bonds in triphenylene (VIII), where the π-bond order are largest in the three bonds surrounding the non-protonated carbons. In coronene (XI) the bond between the two disimilar quaternary carbons also dominates the orientation of σ_{11} which is perpendicular to these bonds for both C_{3a} and C_{3b}. Experimental determinations of the ^{13}C shielding tensors will establish if these theoretical trends are preserved or if errors in the semiempirical method prevent this level of prediction.

The shielding tensors of C_{3a}, C_{3b}, C_{6a} and C_{7b} in X exhibit the near axial symmetry common to many other bridgehead carbons, but the tensor for C_{7a} definitely has a large anisotropy. The ^{13}C shielding tensor of C_{7a} is dominated by the formal C_7–C_{7a} double-bond with σ_{11} lying at 91° from the C_7–C_{7a} bond. The theory indicates a fixed π-bond for C_7–C_{7a} as prescribed by Kekulé structures for X [3]. This structural feature is reflected in the ^{13}C shielding tensor of both C_7 and C_{7a}.

4. Conclusions

Rules have been developed for the orientation of the two in-plane shielding components in terms of the bond-orders of adjacent bonds. The σ_{11} tends to orient along the direction of lowest π-bond character and perpendicular to C–C bonds in which the π-electron density has been localized. Dealing with trigonal carbon atoms requires the final orientation to be a compromise of these principles for all three bonds except where symmetry considerations make two or three of the bonds equal. When two bond orders are equal and larger than the third, σ_{11} lies along the third C–C bond. If the two equal bonds have smaller bond orders, then σ_{11} lies perpendicular to the third bond with the highest bond order. When all three bonds have identical bond orders, an axially symmetric tensor with σ_{11} equal to σ_{22} will be achieved providing long range shielding terms do not introduce minor differences in σ_{11} and σ_{22} and distort the tensor to near axially symmetry.

The relationships between the calculated in-plane shielding components of the ^{13}C shielding tensors in condensed aromatic hydrocarbons and the degree of delocalization of the π-electrons in the adjacent C–C bonds provides a new criteria for studying aromaticity. Unlike properties, such as overall energy, the

^{13}C shielding data provide a way to define aromaticity and electron delocalization for localized molecular segments or even for individual bonds. The measured ^{13}C shielding tensors in condensed aromatic hydrocarbons can become a direct experimental probe of the degree of delocalization of π-electrons.

It should be realized that the results reported here are a preliminary theoretical estimate based on semi-empirical MNDO wave functions. All that should be expected of the MNDO and ΔE approach is that it will faithfully reproduce the principal symmetry features governing chemical shielding and give good estimates of the relative magnitudes of the principal components upon which reasonably reliable orientational features can be based. It is acknowledged that the results reported here are very dependent on the validity of the rather severe ΔE approximation, and if this approximation breaks down significant deviations from the predictions can be expected. Any conclusions on the reliability of this approximation must therefore wait until a sufficiently large body of comparable experiment data are available. The calculations, though approximate, do provide a highly systemized basis for organizing existing and future experimental results, and should stimulate considerable interest in the shielding tensors of the fused aromatic hydrocarbons.

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