*Tetrahedron* Vol. 41, No. 18, pp. 3771 to 3777, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

# BENZANNELATED ANNULENES —12. THEORETICAL STUDY OF GEOMETRIES AND $^1$H CHEMICAL SHIFTS OF BENZANNELATED [14]ANNULENES[1]

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(*Received in Germany* 3 *May* 1985)

Abstract - The geometries and the $^1$H chemical shifts of dihydropyrene 1 and its benzannelated derivatives 2 - 8 have been studied by means of semi-empirical quantum chemical procedures. The calculated bond lengths of 1 and proton shifts of 1 - 5 are in good accord with the corresponding experimental values. We show that monobenzannelation in 2 - 4 causes considerable bond length alternation in the [14]perimeter and hence reduced diatropocity. The same is true for the phenanth-fused dibenzannelated compounds 4 and 7. On the other hand we report evidence that anth-fused dibenzannelated dihydropyrenes 5, 6, and 8 should be characterized by symmetric geometrical structures without significant bond length alternation thus leading to enhanced diatropicity.

Neutral [n]annulenes with n=4m+2 are diatropic[2] which has been rationalized by assuming a diamagnetic ring current (RC) effect[3]. Annelation with other conjugated systems changes the electronic structure and hence the magnetic properties of the annulene. In recent years the annelation effect has been studied extensively[4-9]. In the case of [n]annulenes with small or medium n, non-bonded interaction between the inner protons usually leads to considerable distortion of the perimeter from planarity so that optimal conjugation in the π-system is impossible. On the other hand dihydropyrene 1 and its benzannelated derivatives 2 - 8 constitute suitable models in order to study the benzannelation effect in annulenes, since 1 is essentially planar[10] and 1 - 8 represent conformationally rigid systems. Compounds 1 - 5 were studied experimentally[5-8] and theoretically[9]. Also calculations on magnetic susceptibilities and resonance energies have been reported[11]. In this paper we report on our theoretical studies on the geometries and $^1$H chemical shifts of 1 - 8. Compounds 5, 6, and 8 are of special interest since an odd number of carbon atoms occurs in the [14]perimeter between the two annelating benzene rings so that all Kekulé-Robinson-Clar structures[12] show at least one quinoid 6-ring. Thus 5, 6, and 8 constitute[11] type II systems in contrast to the type I compounds 2 - 4 and 7 which are characterized by at least one Kekulé-Robinson-Clar structure where none of the annelating 6-rings is quinoid. Recently[13] we introduced the term phenanth-fused for type I and anth-fused for type II dibenzannelated [4m+2]annulenes.

The magnitude of the $^1$H chemical shifts in annulenoid systems depends considerably on the extent of bond length alternation (BLA). Therefore the use of ideal geometries (IG) with standard bond lengths is not always a sufficient approximation. We determined the geometries of 1 - 8 by means of the π-SCF force field method (FF) of Lindner[14]. Only the Ohno-Klopman formula[15] for the two-centre electron repulsion integrals has been replaced by the Mataga-Nishimoto formula[16]. This proved necessary since only the latter formula takes sufficiently well into account electron correlation which is crucial in order to obtain the correct delocalized structures for [4m+2]annulenes[17,18]. For example, the unmodified FF procedure[14]

would yield the symmetry reduced solution 1 instead of the delocalized structure 1' (see Fig. 1) which has been found by X-ray analysis[10]. In order to reduce the computing time we chose R=H for 1 - 8 although 2, 4, and 5 have been studied experimentally with R=$CH_3$. However, this should not affect significantly the geometry and the shifts of the protons which are located at the carbon atoms of the π-network as has been verified in case of 1[5,19] and 3[6].

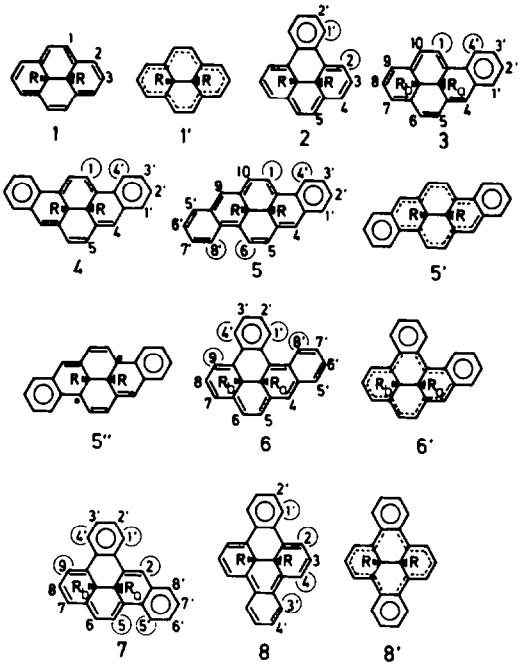


Fig. 1. Survey of compounds under study

The $^1$H chemical shifts δ are calculated according to the procedure of Ref.[20] which leads to shifts in good agreement with experimental values for a large number of conjugated compounds[18,20-22]. The formula used to obtain δ is $\delta=\delta^{RC}+\delta^{LA}+\delta^{o}$, where $\delta^{RC}$ is the RC contribution of the π-system and $\delta^{LA}$ the local anisotropic contribution of π- and σ-system. We have shown[21] that $\delta^{LA}$ is important for a quantitative assessment of proton shifts in annulenoid compounds whereas in case of benzenoid hydrocarbons it is a sufficient approach to take only $\delta^{RC}$ into account. $\delta^{o}$ contains all contributions to δ which do not depend on the topology of the molecule and it defines the zero of the δ-scale. For overcrowded protons, which have been denoted by encircled numbers in Fig. 1, $\delta^{o}$ contains an additional down-field shift (van der Waals correction)[23]. In this work we used the value $\delta^{o}$=5.12 ppm and for overcrowded 6- and 14-ring protons the values 5.80 and 5.24 ppm. The formulae given in Ref.[20] for calculating $\delta^{LA}$ have been derived only for planar systems. Therefore, in case of the hydrocarbons 1 - 8 which are not strictly planar, we calculated $\delta^{LA}$ by assuming planar geometries whose bond lengths have been determined by utilizing the self-consistent resonance (SCβ) procedure[20].

## RESULTS AND DISCUSSION

### Geometries

Similar to dihydropyrene 1, the benzannelated derivatives 2 - 5, 7, and 8 are also essentially planar according to our FF calculations. The maximum deviations from the mean molecular planes are less than 17 pm. The torsions along the bonds in the carbon skeletons of the π-networks are small and so they do not affect appreciably the π-conjugation. The bond lengths which are obtained for planar geometrical models by using the SCβ approach agree well with those of the FF procedure. The maximum differences amount to only 2 pm. Therefore, the electronic structure and hence also the magnetic properties of 2 - 5, 7, and 8 are mainly determined by the extent of BLA which is induced by the annelating benzene rings. Only with 6, the close proximity of the two annelating 6-rings and the resulting important nonbonded interaction between the protons 1' and 8' leads to more pronounced deviations from planarity, see Fig. 2. We calculate a distance

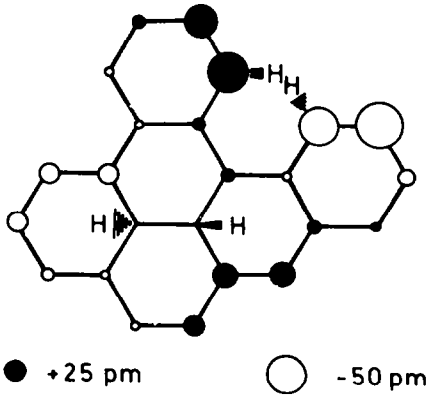


Fig. 2. Calculated deviations of carbon atoms of 6 from the mean molecular plane

of 207 pm between protons 1' and 8' which is similar to that between the overcrowded protons in phenanthrene or perylene[24]. Larger differences between SCβ and FF bond lengths up to 3.5 pm are encountered for 6, especially in the [14]-perimeter around the annelated 6-rings.

We can divide the C-C bonds in 1 - 8 into three classes: short bonds with r<137 pm which we consider as quasi localized double bonds (═══), bonds with 137 pm≤r≤144 pm which we consider as 'aromatic' bonds (╌╌╌), and long bonds with r>144 pm which we consider as quasi single bonds (———). Using the sextet notation[12] for 6-rings where all bonds are aromatic we arrive at the bond lengths pattern for 2 - 4 and 7 displayed in Fig. 1, whereas 1 is characterized by structure 1'. The longest aromatic bonds with r=142.7-143.9 pm are those common to a 6-ring and the [14]perimeter. This is due to a reduction of bond order by annelation[9,25]. The bond lengths pattern for the type II hydrocarbons 5, 6, and 8 is represented by the structures 5', 6', and 8' in Fig. 1. These delocalized structures are obtained irrespective of the starting geometry. The bonds which are common to a 6-ring and the [14]perimeter are even longer (r=144.5-146.3 pm) than in the case of the type I compounds. However, such bonds are still important for the π-conjugation so that 5, 6, and 8 cannot be sonsidered as [22]perimeter systems.

The investigation of the Thouless instability conditions[26] for the wave functions of 1 - 8 revealed that all these compounds are singlet and non-real stable, i.e. the lowest eigenvalues $\lambda^{s}$ and $\lambda^{nr}$ of the singlet and non-real instability problems are well above zero. This means that there exist no other closed shell or complex wave functions which are equal or lower in energy. Furthermore this demonstrates that the obtained delocalized structures 5', 6', and 8' represent indeed more stable solutions than those with second order bond fixation[27] (formulae 5, 6, and 8 in Fig. 1) and in case of 5 or 8 with broken symmetry. The λ values of the type II compounds are slightly lower ($\lambda^{s}\approx1.7$ eV, $\lambda^{nr}\approx1.5$ eV) than those of 1 ($\lambda^{s}=1.9$ eV, $\lambda^{nr}=2.4$ eV) and the type I systems ($\lambda^{s}=\lambda^{nr}=2.4$-2.8 eV). This derives from the smaller energy gap between the highest occupied and the lowest virtual orbital for the type II compounds 5, 6, and 8 with g≅3.8 eV with respect to 1 - 4 and 7 with g=4.8-5.2 eV.

The consideration of Kekulé structures alone does not allow conclusions on the geometrical structure of type II systems 5, 6, and 8, i.e. if they prefer delocalized geometries 5', 6', and 8' or those with one *o*-quinoid benzene ring. This can easily be verified if one calculates the resonance energies by using the method of conjugated circuits[28] since all four Kekulé structures A - D (see Fig. 3 where these are given for 5 as an example) leading to the delocalized structure yield the same resonance energy as the two Kekulé structures A and B alone which correspond to one of the two possible *o*-quinoid geometries.

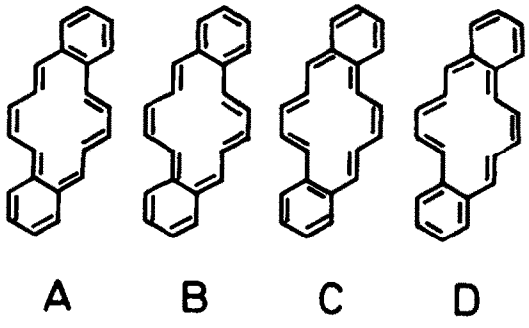


Fig. 3. Kekulé structures of 5 (only the π-network has been given)

## $^{1}$H Chemical Shifts

Calculated and experimental $^{1}$H chemical shifts for 1 - 8 are given in Table 1. The mean absolute error of our calculated values for all protons of 1 - 5 is only 0.14 ppm. The largest errors of maximum 0.4 ppm are encountered with the 6-ring proton 1' of 5 and the 14-ring protons 9 of 3, 4 of 4, and 5 of 5. $\delta^{LA}$ has been calculated for planar geometrical models with SCβ bond lengths which differ slightly from the FF ones. This can lead to errors in the order of 0.1 ppm as can be seen by comparison of the values obtained for the SCβ or FF structure 1' with those obtained for a geometrical model with BLA ($r_{C=C}/r_{C-C}$=134/146 pm). The deviations from planarity should not lead to significant errors in $\delta^{LA}$ except perhaps in case of 6 for overcrowded protons. Furthermore somewhat larger errors are due to the RC term which depends more on variations of bond

Table 1. Calculated ($\delta^{RC}$, $\delta^{LA}$, $\delta$) and experimental ($\delta_{exp}$; R=$CH_3$) $^1H$ chemical shifts of 1-8 (all values in ppm)

| Compound | Proton | $\delta^{RC}$ | $\delta^{LA}$ | $\delta$ | $\delta_{exp}$ | Ref. |
|---|---|---|---|---|---|---|
| 1 | 1 | 2.10 | 1.37 | 8.59 | 8.67 | 7,8 |
| | 2 | 2.00 | 1.36 | 8.48 | 8.62 | |
| | 3 | 1.69 | 1.36 | 8.17 | 8.11 | |
| 2 | 2 | 1.21 | 1.51 | 7.96 | 8.30 | 7 |
| | 3 | 0.86 | 1.38 | 7.36 | 7.25 | |
| | 4 | 0.96 | 1.29 | 7.37 | 7.59 | |
| | 5 | 1.02 | 1.34 | 7.48 | 7.36 | |
| | 1' | 1.37 | 1.57 | 8.74 | 8.81 | |
| | 2' | 1.02 | 1.43 | 7.57 | 7.62 | |
| 3 | 1 | 1.24 | 1.62 | 8.10 | 8.11 | 6,8 |
| | 4 | 1.30 | 1.51 | 7.93 | 7.90 | |
| | 5 | 1.06 | 1.40 | 7.58 | 7.62 | |
| | 6 | 1.00 | 1.31 | 7.43 | 7.52 | |
| | 7 | 0.97 | 1.33 | 7.42 | 7.37 | |
| | 8 | 0.81 | 1.36 | 7.29 | 7.14 | |
| | 9 | 0.94 | 1.27 | 7.33 | 7.70 | |
| | 10 | 1.05 | 1.34 | 7.51 | 7.38 | |
| | 1' | 1.21 | 1.54 | 7.87 | 7.99 | |
| | 2' | 0.97 | 1.43 | 7.52 | 7.69 | |
| | 3' | 1.01 | 1.43 | 7.56 | 7.70 | |
| | 4' | 1.32 | 1.56 | 8.68 | 8.75 | |
| 4 | 1 | 0.87 | 1.64 | 7.75 | 7.40 | 8 |
| | 4 | 0.90 | 1.54 | 7.56 | 7.16 | |
| | 5 | 0.68 | 1.43 | 7.23 | 7.05 | |
| | 1' | 0.99 | 1.57 | 7.68 | 7.58 | |
| | 2' | 0.84 | 1.45 | 7.41 | 7.46 | |
| | 3' | 0.88 | 1.45 | 7.45 | 7.49 | |
| | 4' | 1.07 | 1.58 | 8.45 | 8.25 | |
| 5 | 1 | 2.41 | 1.65 | 9.30 | 9.29 | 8 |
| | 4 | 2.42 | 1.47 | 9.01 | 8.90 | |
| | 5 | 2.25 | 1.42 | 8.79 | 8.39 | |
| | 1' | 1.71 | 1.50 | 8.33 | 8.70 | |
| | 2' | 1.24 | 1.40 | 7.76 | 7.76 | |
| | 3' | 1.31 | 1.41 | 7.84 | 7.80 | |
| | 4' | 1.97 | 1.56 | 9.33 | 9.39 | |
| 6 | 4 | 2.24 | 1.50 | 8.86 | | |
| | 5 | 1.71 | 1.43 | 8.26 | | |
| | 6 | 1.95 | 1.43 | 8.50 | | |
| | 7 | 2.06 | 1.41 | 8.59 | | |
| | 8 | 2.12 | 1.38 | 8.62 | | |
| | 9 | 2.29 | 1.62 | 9.15 | | |
| | 1' | 1.94 | 2.19 | 9.93 | | |
| | 2' | 1.32 | 1.47 | 7.91 | | |
| | 3' | 1.34 | 1.42 | 7.88 | | |
| | 4' | 2.02 | 1.57 | 9.39 | | |
| | 5' | 1.58 | 1.51 | 8.21 | | |
| | 6' | 1.12 | 1.41 | 7.65 | | |
| | 7' | 1.16 | 1.46 | 7.74 | | |
| | 8' | 1.63 | 2.16 | 9.59 | | |
| 7 | 2 | 1.11 | 1.62 | 7.97 | | |
| | 5 | 0.84 | 1.52 | 7.60 | | |
| | 6 | 0.67 | 1.45 | 7.24 | | |
| | 7 | 0.60 | 1.38 | 7.10 | | |
| | 8 | 0.53 | 1.31 | 6.96 | | |
| | 9 | 0.82 | 1.62 | 7.68 | | |
| | 1' | 1.16 | 1.62 | 8.58 | | |
| | 2' | 0.89 | 1.45 | 7.46 | | |
| | 3' | 0.88 | 1.46 | 7.46 | | |
| | 4' | 1.10 | 1.63 | 8.53 | | |
| | 5' | 1.06 | 1.61 | 8.47 | | |
| | 6' | 0.89 | 1.45 | 7.46 | | |
| | 7' | 0.85 | 1.45 | 7.42 | | |
| | 8' | 1.03 | 1.53 | 7.68 | | |
| 8 | 2 | 2.35 | 1.61 | 9.20 | | |
| | 3 | 1.83 | 1.40 | 8.35 | | |
| | 1' | 2.04 | 1.60 | 9.44 | | |
| | 2' | 1.33 | 1.41 | 7.46 | | |

lengths than $\delta^{LA}$. $\delta^{RC}$ values obtained with the SCβ and FF geometry differ in the mean by 0.15 ppm and the maximum 0.3 ppm. Only in case of the overcrowded protons 1' and 8' of 6 the SCβ approach leads to exaggerated RC effects due to unrealistic small non-bonded distances in the assumed planar geometry. Consequently the actually encountered errors of our calculated shifts are in the expected order of magnitude. It might be possible that larger errors occur for the overcrowded protons of the yet unknown 6 since the size of $\delta^{RC}$ and the van der Waals correction in $\delta^{O}$ depends strongly on the orientation of the C-H bond to other C-H and C-C bonds[23]. However, we expect that our calculated shifts for the non-overcrowded protons of 6 and for all protons of 7 and 8 are reliable similarly to those of 1 - 5.

For all benzannelated compounds 2 - 5 the order of the 6-ring protons is correctly reproduced by our calculations. This applies as well to the 14-ring protons of 4 and 5, whereas protons 4/5 of 2 are interchanged and proton 9 of 3 is calculated at too high a field and proton 10 of 3 at too low a field.

In the calculation of proton shifts of 1 - 8 the inductive and hyperconjugative effect of the alkyl bridges was not taken into account. Both should influence the electronic structure of the [14]perimeter similarly[29]. In order to see how the bridges affect the proton shifts we simulated the inductive effect within the SCβ approach by increasing the core energy by 1.4 eV (this value describes best the alteration of ionization energies in the series of methylbenzenes) of those carbon atoms which are connected by the alkyl bridges. As expected the shifts of the 6-ring protons decrease only slightly by about 0.02 ppm. However, the 14-ring protons also experience only small shifts of about 0.06 ppm to higher field and the shift is nearly the same for all these protons.

Similarly as with benzenoid hydrocarbons[20] $\delta^{RC}$ and $\delta$ (not including the van der Waals correction) for 1 - 8 correlate well. Thus the order of the protons is generally already determined by $\delta^{RC}$, exceptions constitute protons 1 and 4 of 3 - 5, protons 5 and 9 of 7 and some protons of 6.

The proton shifts which are calculated for the FF geometries 5' and 8' of the type II annulenes 5 and 8 deviate in the mean by only 0.06 ppm and not more than 0.18 ppm from those

which are obtained by using an IG with all bond lengths fixed at 140 pm, see Table 2. This shows that also the long bonds which are common to 6- and 14-ring in 5, 6, and 8 are important for the magnetic properties so that these compounds cannot be considered simply as [22]perimeter systems. Proton shifts at significantly higher field are obtained if 5 and 8 are characterized by the unsymmetrical structures given in Fig. 1 ($r_{C=C}/r_{C-C}/r_{C\equiv\equiv C}$=134/146/140 pm). Furthermore protons which are equivalent in the delocalized structures 5' and 8' (e.g. protons 1 and 6 of 5) show values being different up to 0.28 ppm (14-ring) or even 0.54 ppm (6-ring). This demonstrates that the shifts of the protons at the annelated benzene rings represent s en sitive probes for the electronic structure of the [14]perimeter similar to the coupling constants[30]. A fast dynamical process interchanging the two quinoid structures for 5 and 8 would lead to averaged shifts for corresponding protons (e.g. 1 and 6, 4 and 9, etc. in 5), however, with significantly smaller δ values than those which are calculated for the delocalized structures 5' and 8' and which are observed experimentally. This gives further reason to assume a symmetric delocalized geometry 5' and 8' in solution of 5 and 8.

Table 2. Calculated $^1$H chemical shifts δ (in ppm) for 5 and 8 assuming ideal geometry (IG), calculated π-SCF force field geometry (FF) or asymmetric structures (AS), and experimental results (EXP) for 5 (R=$CH_3$)[8]

| Compound | Proton | IG | FF | AS | EXP |
|---|---|---|---|---|---|
| 5 | 1 | 9.29 | 9.30 | 8.33 | 9.29 |
| | 6 | 9.29 | 9.30 | 8.20 | 9.29 |
| | 4 | 8.98 | 9.01 | 8.17 | 8.90 |
| | 9 | 8.98 | 9.01 | 7.89 | 8.90 |
| | 5 | 8.74 | 8.79 | 7.79 | 8.39 |
| | 10 | 8.74 | 8.79 | 7.87 | 8.39 |
| | 1' | 8.35 | 8.33 | 8.02 | 8.70 |
| | 5' | 8.35 | 8.33 | 7.48 | 8.70 |
| | 2' | 7.85 | 7.76 | 7.65 | 7.76 |
| | 6' | 7.85 | 7.76 | 7.18 | 7.76 |
| | 3' | 7.89 | 7.84 | 7.68 | 7.80 |
| | 7' | 7.89 | 7.84 | 7.22 | 7.80 |
| | 4' | 9.52 | 9.33 | 8.95 | 9.39 |
| | 8' | 9.52 | 9.33 | 8.51 | 9.39 |
| 8 | 2 | 9.21 | 9.20 | 8.34 | |
| | 4 | 9.21 | 9.20 | 8.11 | |
| | 3 | 8.26 | 8.35 | 7.52 | |
| | 1' | 9.54 | 9.44 | 9.01 | |
| | 3' | 9.54 | 9.44 | 8.50 | |
| | 2' | 7.94 | 7.86 | 7.71 | |
| | 4' | 7.94 | 7.86 | 7.24 | |

With the type I annulenes 2 - 4 and 7 the BLA in the [14]perimeter which is induced by the annelating benzene rings leads to the expected decrease of the diamagnetic RC effect. No significant BLA is found in the case of the type II compounds 5, 6, and 8 and hence we observe shifts for the protons of the 14-ring similar to those in 1. For benzene we calculate δ=7.20 ppm which is only slightly smaller than the experimental value[31] $\delta_{exp}$=7.27 ppm. In a 6-ring with bond lengths as those occuring in the annelated benzene rings of 2 - 8 we calculate shifts δ≤7.23 ppm and only for an overcrowded proton is δ≤7.91 ppm obtained. Thus the shifts of all protons of the 6-rings of 2 - 8 are at lower field than in an isolated 6-ring. This reflects the influence of the outer [18]- or [22]perimeters, although the electronic structure is not dominated by them. The outer perimeter influence turns out to be more important in case of the type II compounds 5, 6, and 8 as can be seen by comparing corresponding ring protons. This is due to the characteristic differences in the bond lengths pattern of type I and II annulenes.

Thus far we have discussed only the shifts of protons on the periphery of the system. For the internal protons located at the alkyl bridges we can calculate only the $\delta^{RC}$ term. We computed $\delta^{RC}$ for the proton at the bridges with R=H since we can assume that the RC effect will influence protons at the alkyl bridges with R=$CH_3$ and R=H similarly. Our calculated $\delta^{RC}$ values correlate sufficiently well with the experimental shifts for the methyl protons of 1 - 5 with R=$CH_3$, see Table 3. The regression line is

$$\delta_{calc} = 0.852\ \delta^{RC} + 0.79 \qquad (1)$$

which yields shifts for the methyl protons of the yet unknown compounds 6 - 8 similar to those which have been obtained by a different semiempirical approach[9]. Similar to 1 - 5 also for 6 - 8 the high field shifts due to the RC effect turn out to be considerably larger for the type II systems 6 and 8 than those for the type I annulene 7.

## CONCLUSION

In this work we have determined the geometries and $^1$H chemical shifts of the dihydropyrene 1 and its benzannelated derivatives 2 - 8 by means of semiempirical procedures. The agreement between calculated and experimental bond lengths for 1 and proton shifts for 1 - 5

Table 3. Calculated RC contribution $\delta^{RC}$ of the internal proton of 1 - 8 (R=H) and calculated ($\delta_{calc}$) and experimental ($\delta_{exp}$) proton shifts for the methyl protons of 1 - 8 (R=$CH_3$). All values are given in ppm

| Compound | $\delta^{RC}$ | $\delta_{calc}$ [a] | $\delta_{calc}$ [b] | $\delta_{exp}$ | Ref. |
|---|---|---|---|---|---|
| 1 | -5.78 | -4.13 | -4.42 | -4.25 | 5,6 |
| 2 | -2.57 | -1.40 | -1.80 | -1.85 | 5,7 |
| 3 | -2.58 [c] | -1.41 [c] | -1.86 | -1.60 | 5-7 |
| | -2.62 | -1.44 | | | |
| 4 | -1.41 | -0.41 | 0.04 | 0.02 | 5,8 |
| 5 | -5.48 | -3.88 | -3.22 | -3.58 | 5,8 |
| 6 | -5.26 [c] | -3.69 [c] | -3.43 | | |
| | -5.18 | -3.62 | | | |
| 7 | -1.34 [c] | -0.35 [c] | -0.10 | | |
| | -1.40 | -0.40 | | | |
| 8 | -5.45 | -3.85 | -3.31 | | |

[a] Calculated by means of the regression line (1). [b] Taken from Ref. 8. [c] First value for proton $H_a$, second value for proton $H_b$, see Fig. 1.

is satisfying. Our study shows that benzannelation in the type I compounds 2 - 4 and 7 induces BLA in the [14]perimeter leading to a reduction of diamagnetic RC effects. On the contrary the type II systems 5, 6, and 8 are characterized by geometrical structures without appreciable BLA if we disregard the long aromatic bond common to two fused rings. These annulenes constitute together with the parent annulene 1 delocalized ('aromatic') conjugated π-networks exhibiting similar shifts of the 14-ring protons. Furthermore the 6-ring protons of the type II systems appear at significantly lower field than those of the type I compounds.

Structures with an *o*-quinoid benzene ring in 5, 6, and 8 would lead to significantly smaller shifts thus excluding the possibility of fluctuating systems. But we want to stress that type II annulenes need not to be necessarily delocalized systems. Especially for more extended type II annulenes it becomes more likely to encounter wave functions with broken symmetry or *o*-quinoid benzene rings which are more stable than the delocalized structures. In case of the benzannelated annulenes 2 - 8 significant differences in geometry and proton shifts are observed between systems of different type whereas those between isomeric compounds of the same type are small.

In the $^1$H NMR spectra of the type I compounds 2 - 4 ordinary line widths under 2 Hz are encountered. On the other hand quite large line widths of about 7 Hz are found in the case of the type II compound 5. Furthermore the signals of 5 broaden at lower temperature and even an almost collapse of signals is observed indicating the presence of a triplet species for which we proposed[8,13] a biradical form 5'' of 5 (see Fig. 1). π-SCF calculations with subsequent configuration interaction between singly excited configurations have shown[13] that the energy separation between the restricted Hartree-Fock ground state and the lowest triplet state is considerably lower with the type II than with the type I systems.

The investigation of the Thouless instability conditions[26] for 1 - 8 revealed that all compounds are non-singlet (triplet) unstable since the lowest eigenvalue $\lambda^{ns}$ of the non-singlet instability problem is negative. This proves the existence of an unrestricted Hartree-Fock solution which is lower in energy than the restricted one. However, this is not tantamount to a triplet ground state since electron correlation generally stabilizes the singlet Hartree-Fock wave function more than the triplet state. But the occurence of non-singlet instabilities underlines the importance of spin correlation in these conjugated annulenoid systems and demonstrates that a treatment of triplet states and their energies with respect to the lowest singlet state is possible only by inclusion of additional configuration interaction for all states.

We are currently attempting to synthesize 8 and several related benzannulenes, in an attempt to more clearly delineate the properties of these interesting anth-fused hydrocarbons, and provide further tests for the chemical shift predictions presented in this paper.

Acknowledgement - We would like to thank Professor H. J. Lindner for supplying his π-SCF force field program PIMM. H. V. thanks the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and the Fonds der Chemischen Industrie, Frankfurt/Main, for financial support. The calculations were performed in the Universitätsrechenzentrum Heidelberg on the IBM 370/168 and 3081 D.

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