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MAGNETIC SUSCEPTIBILITIES OF SOME DEHYDRO[12]ANNULENES

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Abstract—The magnetic susceptibilities χ and exaltations Λ of the dehydro[12]annulene **1** and its benzannelated derivatives **2–4** have been calculated by means of a modified Hückel theory taking into account ring-current (RC) and local contributions (LC) $\chi^{\rm RC}$ and $\chi^{\rm LC}$ to χ. For **4** the experimental χ value could be determined. The calculated $\chi^{\rm RC}$ and Λ values indicate the anti- or nonaromatic nature of these diamagnetic compounds. The antiaromatic character of the 12-perimeter in **2–4** does not depend significantly on the number of annelated benzene rings. Furthermore the range of applicability of the Hückel theory for calculating magnetic susceptibilities of conjugated hydrocarbons with sp^2- and sp-hydridized carbon atoms is discussed.

The magnetic susceptibilities χ of many organic compounds can be calculated with atomic or bond increments.[1] Such increments are local parameters which do not depend on the topology of the molecule. In the case of planar cyclic conjugated compounds the description of χ by increment systems is generally no longer possible. Instead we can write $\chi = \chi^{\rm RC} + \chi^{\rm LC}$ with the local contribution (LC) $\chi^{\rm LC}$ and the ring-current (RC) contribution $\chi^{\rm RC}$. $\chi^{\rm LC}$ is independent of the topology of the molecule whereas the sign and magnitude of $\chi^{\rm RC}$ changes with the size and type of the conjugated cycles, e.g. $\chi^{\rm RC} > 0$ for (4n+2)annulenes and the opposite applies for (4n)annulenes (throughout this communication all susceptibilities are given in unrationalized cgs-emu units of $-10^{-6}\,{\rm cm^3\,mol^{-1}}$). Positive (negative) $\chi^{\rm RC}$ values are associated with a diamagnetic (paramagnetic) RC effect.

Dauben *et al.*[2] introduced the exaltation $\Lambda = \chi - \chi^{\rm IN}$ as a measure of the aromaticity of a conjugated compound where $\chi^{\rm IN}$ is the susceptibility calculated from increments by means of a localized multiple bond model. Due to the Λ-criterion compounds can be classified as aromatic ($\Lambda \gg 0$), nonaromatic ($\Lambda \cong 0$), or antiaromatic ($\Lambda \ll 0$).

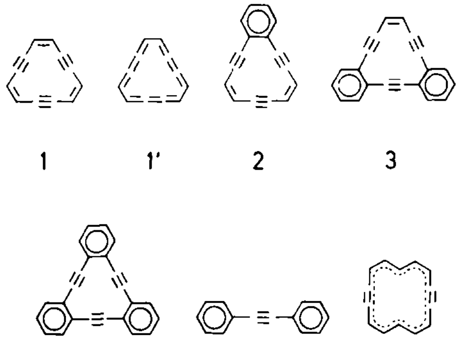

Fig. 1. Survey of compounds under study.

Correspondingly (4n)annulenes should be antiaromatic and (4n+2)annulenes aromatic tantamount to the para- and diatropicity of their ^{1}H-chemical shifts.[3] To the best of our knowledge a negative exaltation of a (4n)-annulene has been found only for [16]annulene.[2] However, this annulene is not planar[4] due to steric repulsions between the inner hydrogen atoms. On the other hand, dehydro[4n]annulenes are mostly planar which facilitates the analysis of magnetic susceptibilities.

In this communication we present a theoretical study of the trisdehydro[12]annulenes **1**,[6] **2**, **3** and **4**.[7] Furthermore the experimental χ value of **4** is reported. These four dehydro[12]annulenes differ in the number of annelated benzene rings. Therefore **1–4** are suitable models for the study of the benzannelation effect which was investigated so far only by means of ^{1}H-chemical shifts.[8] However, conclusions about the annulenoid character of **1–4** are easier to obtain from magnetic susceptibilities than from proton shifts since the latter are no global property of the molecule and depend considerably on the local anisotropy of the neighbourhood of the proton in question. Furthermore **1–4** do not possess protons common to all four compounds. The Λ-criterion provides a classification scheme due to the aromaticity of the molecule as a whole. Conclusions about the annulenoid aromaticity of the 12-perimeter in the systems **2–4** can be derived from the annulenoid exaltation $\Lambda_{12} = \Lambda - m\Lambda_6$ where Λ_6 is the exaltation of benzene and m the number of annelated benzene rings.

COMPUTATIONAL PROCEDURE

The modified Hückel molecular orbital (MHMO) procedure of Amos and Roberts[9] is utilized for the calculation of $\chi^{\rm RC}$. The standard resonance integral $\beta_0 = -4.15\,{\rm eV}$[10] is used whereas we have chosen $\lambda = 0.59$ since it gives a better agreement with experiment and guarantees $\chi^{\rm RC} \cong 0$ for noncyclic polyenes.[12] $\chi^{\rm LC}$ is calculated with the atomic increments for C_{sp^2} and H given in ref. 13 whereas the increment for C_{sp} will be reported in the next section. $\chi^{\rm IN}$ is obtained using the bond increment system suggested by Haberditzl.[1,14] The $\chi^{\rm IN}$

values are uncertain within ±0.4 per triple bond since only an increment for C_{sp^3}–C_{sp} but not for C_{sp^2}–C_{sp} is given.[1,14]

The resonance integrals β_{st} between bonded atoms s and t are treated as functions of the atomic distances r_{st},[15] $\beta_{st} = \beta_0 \exp\{\kappa(r_0 - r_{st})\}$, where $r_0 = 1.397$ Å and $\kappa = 4$ Å^{-1}. The rather large κ value (see ref 16) is necessary in order to introduce a realistic bond order alternation in **1**–**4** as well as double bond localization in a large series of benzannulenes.[17] The bond lengths are taken from the experimental X-ray structures of **4**[18] and **5**.[19] The same geometrical data are employed for **1**–**3** which is justified according to π-SCF calculations[20] where not only the π-system but also the π'-system formed by the sp-hybridized carbon atoms in the molecular plane is explicitely taken into account.

RESULTS AND DISCUSSION

All calculated and experimental susceptibilities and exaltations are given in Table 1. The comparison of calculated and experimental χ of **5** provides us with the missing atomic increment of a sp-hybridized carbon atom, i.e. $\chi_{C_{sp}} = 8.05$. The exaltation Λ of **5** is smaller than twice that of benzene, $\Lambda - 2\Lambda_6 = -4.8$, which indicates the slightly reduced aromaticity of the benzene rings in **5** due to the triple bond. The contribution of the triple bond to χ in **1** is given as $2\ \chi_{C_{sp}} = 16.1$ being already 14% of the total χ. Therefore errors in our $\chi_{C_{sp}}$ value would show up quite considerably in the dehydro[12]annulenes **1**–**4** with three triple bonds. The good agreement between calculated and experimental χ value for **4** (both are identical within the experimental error limit) demonstrates on the one hand that our $\chi_{C_{sp}}$ is accurate enough and on the other that our numerical procedure is applicable to systems like those studied in this communication.

The negative χ^{RC} values of **1**–**4** indicate the expected paramagnetic RC effect. With more and more benzannelation χ^{RC} and hence χ increases. However, it should be emphasized that an increase of χ^{RC} and χ does not necessarily imply the interruption of the 12-perimeter conjugation due to the annelated benzene rings which yield diamagnetic contributions to χ. The annulenoid exaltation Λ_{12} of **1**–**4** is negative indicating the antiaromatic character of the 12-perimeter. The approximate constancy of Λ_{12} in the series **2**–**4** clearly reveals that the increase of χ^{RC} is solely due to the contributions of the benzene rings. According to the total exaltations Λ only the dehydro[12]annulene **1** can be classified as antiaromatic whereas **2**–**4** are nonaromatic annulenoid systems where the aromatic character of the annulene part is masked by the diamagnetic benzene units. A similar behaviour was encountered with benzo[14]- and benzo[18]annulenes.[17]

In our calculations only the non-local anisotropic effect was taken into consideration by means of χ^{RC}. It was shown that local anisotropic (LA) effects of the σ-, π- and in the case of compounds with sp-hybridized atoms also of the π'-system are of great importance for the ^{1}H-chemical shifts especially with annulenoid systems.[5,20,21] In analogy to the theory developed for the calculation of proton shifts[5] we can calculate the magnetic susceptibility as $\chi = \chi^{RC} + \chi^{LA} + \chi^{AT} \cdot \chi^{AT}$ contains all terms which do not depend on the topology of the molecule and can be written as a sum of Pascal constants[22] similar to χ^{LC}. χ^{LA} contains only paramagnetic contributions and is given as

$$\chi^{LA} = (e\hbar/mc)^2(2/3\Delta E)\Big\{\sum_{s}^{(sp)} P_{ss}(1 - P_{s's'}) + \sum_{s-t}^{(sp)}\sum^{(sp)} (P_{st} + P_{s't'} - 2P_{st}P_{s't'}) + (\surd 3/2)\sum_{s-t}^{(sp)}\sum^{(sp^2)} P_{st} + (4/3)\sum_{s-t}^{(sp^2)}\sum^{(sp^2)} P_{st}\Big\}. \tag{2}$$

Here ΔE is a mean excitation energy (we fix $\Delta E = 10$ eV[5]), P_{st} and $P_{s't'}$ are the bond orders between the π- and π'-basis functions at the bonded atoms s − t. The summations run over sp^2- or sp-hybridized atoms.

In the case of hydrocarbons with no sp-hybridized carbon atoms χ^{LA} reduces to

$$\chi^{LA} = (e\hbar/2m)^2(8/9\Delta E)\sum_{s-t}^{(sp^2)}\sum^{(sp^2)} P_{st} \tag{2}$$

which was already derived by Ferguson and Pople.[23]

Table 1. Calculated and experimental magnetic susceptibilities χ and exaltations Λ (all values in units of -10^{-6} cm^3/mol)

Compound	χ^{RC}	χ	χ^{IN}	χ^{LA}	$\chi^{LA\ a}$	$\Lambda_{12}^{\ b}$	Λ	χ_{exp}
1	-176.7	64.2	83.7	-24.0	-24.0	-19.5	-19.5	
2	-131.8	104.1	120.8	-12.8	-13.8	-16.7	-2.5	
3	-92.3	142.2	157.9	-21.2	-21.5	-15.7	-1.5	
4	-56.1	179.2	195.0	-29.7	-29.3	-15.8	-1.6	176.6
5	15.0	115.9	92.3	-38.0	-37.1		23.6	119.5[c]

[a] Calculated with $\chi^{LA}_{C_{sp}} = -0.36$ and $\chi^{LA}_{C_{sp^2}} = -1.94$.

[b] Calculated with $\Lambda_6 = 14.2$ for benzene.

[c] Ref.[25]

Furthermore for alternant hydrocarbons χ^{LA} correlates extremely well with the total π-electron energy and the number of carbon atoms. Consequently χ^{LA} can be written as a sum of Pascal constants and the success of approaches[9,13] based on $\chi = \chi^{RC} + \chi^{LC}$ with $\chi^{LC} = \chi^{AT}$ in that class of compounds is plausible.

We calculated the χ^{RC} and χ^{LA} values of **1–5** with the aid of the extended π-SCF procedure of ref 5. These χ^{RC} values are very similar to those of the MHMO method and we need not discuss them any further. The χ^{LA} values are given in Table 1. They are numerically not small but can nevertheless be approximated as a sum of atomic paramagnetic increments $\chi^{LA}_{C_{sp}}$ ($\chi^{LA}_{C_{sp^2}}$) for the $n_{C_{sp}}$ ($n_{C_{sp^2}}$) sp(sp^2)-hybridized carbon atoms. This derives from the highly localized and isolated nature of the triple bonds in **1–5** so that $P_{s't'} = P_{s's'} = 1$ and (1) reduces to an expression which is dominated by (2) and all other terms depend approximately only on the number of triple bonds. Therefore the magnetic susceptibilities of **1–5** can be calculated satisfactorily from RC and atomic contributions. This might be no longer valid in the case of dehydroannulenes with cumulated double bonds as for example the valence isomer **1'** of **1**; **1'** is neither a minimum on the potential hypersurface of $C_{12}H_6$[24] nor does it contribute significantly as a resonance structure to the groundstate of **1**. Taking standard bondlengths[20] we calculate $\chi^{LA} = -13.9$ for **1'** which is numerically much smaller than the corresponding value for **1**. Obviously an atomic increment system cannot describe the LA contributions in **1'** and this applies to all dehydroannulenes with cumulated double bonds or an electronic structure which cannot be described adequately by cumulated double bonds or localized triple bonds as for example with the dehydro[14]annulene **6**.[20] The paramagnetic RC is greater in **1'** than in **1** as was already demonstrated with ^{1}H-chemical shifts[20] since the multiple bonds are less localized.

CONCLUSION

In this work we obtained the magnetic susceptibilities χ and exaltations Λ of the dehydro[12]annulenes **1–4** by means of the MHMO method[9] with variable resonance integrals. The calculation reproduces the experimental χ of **4** if we use the atomic increment for the sp-hybridized carbon atom which was determined from **5**. Although **1–4** are diamagnetic compounds they are classified as anti- (**1**) or nonaromatic (**2–4**) according to the Λ-criterion. The newly defined exaltation Λ_{12} reveals the antiaromatic annulenoid character of all studied[12]annulenes. The antiaromaticity of the 12-perimeter is nearly independent of the number of annelated benzene rings since these do not introduce significant further localization of the multiple bonds due to the highly localized nature of the triple bond in these compounds. The negligible exaltations of **2–4** are not associated with vanishing RC effects, the same conclusion applies to the ^{1}H-chemical shifts in the olefinic range in such compounds.[20]

The good reproduction of magnetic susceptibilities χ of **4** and **5** by our numerical procedure and most likely also of **1–3** where experimental values are not available derives from two features of these systems, firstly they are not too extended conjugated hydrocarbons,[12] and secondly sp-hybridized carbon atoms occur only in highly localized bonds. Although a Hückel theory can be formulated for planar conjugated compounds with sp- and sp^2-hybridized atoms[26] such an approach will be useful for the calculation of susceptibilities of dehydroannulenes which are not adequately described by isolated triple bonds only if the LA contributions are calculated by means of (1). Unfortunately no experimental data are known in order to test such a model.

EXPERIMENTAL

The magnetic susceptibility of carefully-purified **4** was determined with the magnetic balance employing the Faraday method. A thorough description of the experimental equipment was given in ref 27. All measurements have been repeated at different temperatures (between 4.22 and 308.3 K) and magnetic fields (between 3.5 and 13.1 kG). The maximum total error in the experimental susceptibility amounts to $\simeq 2\%$.

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