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Conference Paper

Zero-Field Splitting Parameters D of Macrocyclic Systems*

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The triplet zero-field splitting parameters D of $[4n]$ - and $[4n + 2]$ -annulenes are calculated within a π -model. The dependence of D on n and the degree of bond lengths alternation is compared with that of ground state properties like magnetic ring currents. Furthermore it is shown that corannulenes which consist of two concentric perimeters with connecting radial bonds cannot be regarded as macrocyclic annulenic systems in the triplet state.

INTRODUCTION

There is considerable interest in the chemical and physical properties of annulenes¹, i. e. completely conjugated monocarbocyclic polyenes, the ring size being indicated by a number in brackets. It is well known that $[4n + 2]$ - and $[4n]$ annulenes can be classified as aromatic and antiaromatic concerning their groundstate stabilities² and magnetic properties as proton chemical shifts^{1,3} or diamagnetic exaltations⁴. Corannulenes⁵ consists of two perimeters which are connected by radial bonds. Considering benzenoid alternant corannulenes the inner and the outer annulene are always of the same type and differ by 12 carbon atoms. Up to now only three members of this class of compounds have been synthesized, i. e. pyrene, coronene and kekulene⁶ (C0214, C0618 and C1830a of Figure 1).

The zero-field splitting (ZFS) parameter D is a measure of the magnetic dipole-dipole interaction of the two unpaired electrons of the triplet state⁷. In planar hydrocarbons $D \sim \langle r^2 - 3z^2/r^5 \rangle$ where r is the distance between the unpaired electrons and z is the axis perpendicular to the molecular plane. Thus D values which can be obtained by EPR⁸ or ODMR⁹ methods provide a useful tool for the study of the electronic properties of planar conjugated systems in the triplet state. Since hitherto no experimental D values of annulenes (except benzene) and corannulenes (except pyrene, coronene and kekulene) have been published we present in this paper a theoretical study of this observable for the compounds given in Figure 1.

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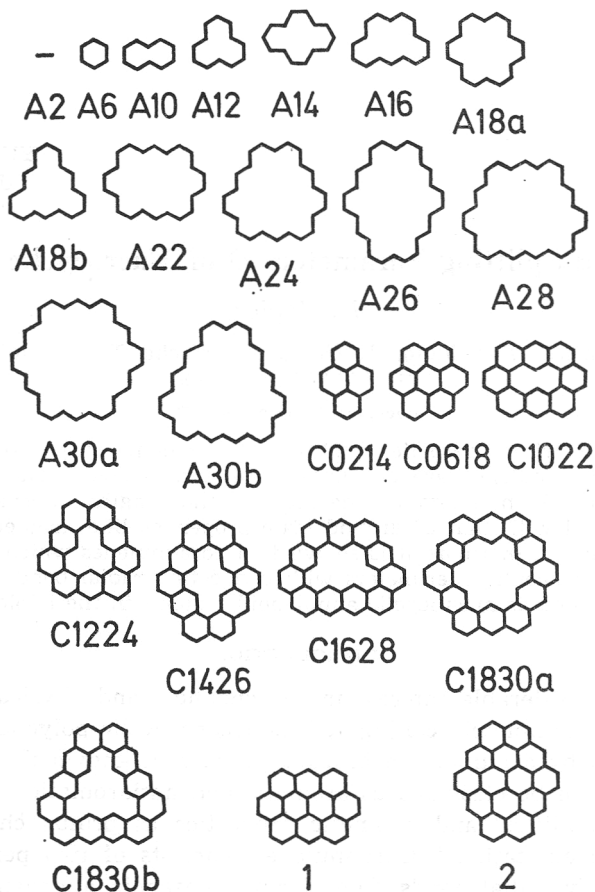


Figure 1. Survey of studied annulenes A_i , corannulenes C_{ij} , and related compounds. Only the carbon skeleton has been given.

THEORETICAL

The triplet wavefunction with lowest energy has been obtained as a linear combination of all singly excited triplet configurations applying the PPP-approximation¹⁰ using standard geometries with all bondlengths fixed at 1.397 Å. Since we are dealing with alternant hydrocarbons there are plus and minus triplet states¹⁰. The triplet state of interest, i. e. that with lowest energy, belongs, however, in all studied cases to the plus type. The ZFS parameter D is simply calculated as $D = \sum_{s < t} \sum f_{st} \mathbf{D}_{st}$ where the summation extends over all pairs of atoms. Details about the used PPP-parameters and the specific form of the coefficients f_{st} which depend on the triplet wavefunction and the two-center integrals \mathbf{D}_{st} can be found elsewhere¹¹. This method has proven very successful in the case of benzenoid hydrocarbons where the absolute average error in the computed D values was only 0.004 cm⁻¹. These errors are due to the approximate nature of the theoretical approach and to the neglect of the fact that ZFS parameters correspond to geometries in the triplet

states potential minima. Since double bond fixation is important for the chemical and physical properties of annulenes we simulate bondlengths alternation by varying the resonance integrals β according to the formula (cf. reference 3a) $\beta = \beta_0(1 + \lambda)^{\pm 1/2}$ where the plus (minus) sign is taken for a formal double (single) bond. β_0 is the resonance integral for the standard bondlength¹¹ and $\pm\lambda$ corresponds to the change in the bondorders.

ANNULENES

Let us first consider the excitation energies T_1 from the groundstate to the triplet state of interest. Since the calculated T_1 corresponds to a vertical transition we can expect that in general experimental T_1 values will be a little lower. As we see in Table I T_1 increases with λ . For $[4n+2]$ annulenes the effect of bondlengths alternation becomes greater with increasing n , whereas for $[4n]$ annulenes the effect of λ does not depend significantly on n . Furthermore T_1 decreases with increasing n for $[4n+2]$ annulenes and the opposite is found for $[4n]$ annulenes. Thus for $\lambda \approx 0.3-0.4$ the T_1 values of $[4n+2]$ - and $[4n]$ annulenes are practically identical if n is sufficiently large. Since the experimental value of T_1 for ethylene A2 is¹² 4.3-4.6 eV we can conclude that $\lambda \approx 0.3-0.4$ corresponds to a highly localized double bond with a π -bond order near 1. The comparison of the isomers A18a/A18b and A30a/A30b shows that T_1 is approximately the same for a given n irrespective of the actual geometry of the molecule, as long as it is planar and sufficiently large to prevent large interactions between nonbonded atoms.

TABLE I

Calculated T_1 Values (in eV) of Annulenes as a Function of the Alternation Parameter λ

Compound ^a	λ				
	0.	0.1	0.2	0.3	0.4
A2	3.63	3.88	4.12	4.36	4.58
A6 ^b	4.05	4.08	4.15	4.25	4.37
A10	2.36	2.42	2.56	2.75	2.96
A14	1.48	1.62	1.88	2.18	2.47
A18a	0.96	1.26	1.63	1.98	2.33
A18b	0.98	1.26	1.61	1.96	2.31
A22	0.64	1.10	1.52	1.91	2.27
A26	0.40	1.03	1.47	1.88	2.26
A30a	0.23	0.99	1.45	1.87	2.25
A30b	0.24	0.99	1.45	1.87	2.25
A12		0.42	0.96	1.44	1.87
A16		0.62	1.17	1.65	2.08
A24		0.85	1.38	1.83	2.23
A28		0.90	1.41	1.85	2.24

^a Cf. Figure 1. ^b PPP-parameters have been chosen as to reproduce the experimental value of benzene A6, cf. reference 11.

TABLE II
 Calculated ZFS Parameters D (in cm^{-1}) of Annulenes as a Function of the
 Alternation Parameter λ

Compound ^a	λ				
	0.	0.1	0.2	0.3	0.4
A2	0.171 ^b				
A6	0.159 ^c	0.159	0.160	0.161	0.162
A10	0.122	0.123	0.127	0.130	0.134
A14	0.095	0.102	0.111	0.117	0.121
A18a	0.084	0.100	0.109	0.115	0.120
A18b	0.081	0.095	0.104	0.110	0.115
A22	0.076	0.097	0.106	0.112	0.117
A26	0.070	0.096	0.104	0.111	0.116
A30a	0.065	0.095	0.103	0.110	0.115
A30b	0.065	0.095	0.103	0.110	0.115
A12		0.099	0.103	0.106	0.110
A16		0.092	0.098	0.104	0.110
A24		0.091	0.101	0.109	0.115
A28		0.092	0.102	0.109	0.115

^a Cf. Figure 1. ^b Value independent of λ . ^c Experimental value¹³ 0.159 cm^{-1} .

A qualitative similar dependence on λ , n and the type of the annulene is found for the ZFS parameter D , cf. Table II. D increases for all annulenes with λ . This derives from the fact that a localized double bond exhibits the highest possible D value for hydrocarbons. The increase in D is more pronounced with large n than with small n . Since $D \sim \langle r^{-3} \rangle$ one expects that D decreases with increasing size of the annulene as is verified for the $[4n+2]$ annulenes. In analogy to T_1 D should increase with n for $[4n]$ annulenes. We find, however, for a given λ a D value which is constant within 0.005 cm^{-1} . Obviously the expected increase is counter-balanced by the enhanced probability in the larger annulene for the unpaired electrons to have a greater average separation. The D values of $[4n+2]$ - and $[4n]$ annulenes with $n > 2$ are all of the same order of magnitude for a given $\lambda \geq 0.1$, the maximum difference is 0.011 cm^{-1} . Only for $\lambda < 0.1$ the differences become larger. Since $D(\lambda = 0.1) \ll D(\lambda = 0.4)$ for all annulenes with $n > 2$ this ZFS parameter should be a very sensitive test for bondlengths alternation in the triplet state. Thus we expect that $D = 0.08\text{--}0.09$ cm^{-1} for A18a and $D = 0.11\text{--}0.12$ cm^{-1} for A14 if we assume that double bond fixation in both annulenes in the triplet state is of the same order of magnitude as in the groundstate¹⁴. However, let us emphasize that we don't know yet the effect of distortions from the planarity on the ZFS parameters.

It is interesting to compare the course of T_1 and D with that of the magnetic ring current which is responsible (at least in a qualitative sense, cf. reference 14) for the typical magnetic properties of annulenes like proton chemical shifts or susceptibilities. The ring current is considerably reduced with increasing λ for all $[4n]$ annulenes and for $[4n+2]$ annulenes only if n is

sufficiently large, cf. reference 3a. The same behavior was found for T_1 and D , however, ring currents have opposite sign for $[4n]-$ and $[4n+2]$ annulenes leading to para- and diatropicity¹, whereas T_1 and D are positive for both types of annulenes. But for a fixed λ and with increasing n the T_1 and D values of $[4n+2]$ annulenes converge to the same limit as $[4n]$ annulenes from opposite directions as found with ring currents.

CORANNULENES AND RELATED COMPOUNDS

Experimental and calculated T_1 and D values of corannulenes C_{ij} with an inner $[i]-$ and an outer $[j]$ annulene and of the related hydrocarbons 1 and 2 are given in Table III. The agreement between calculated and experimental

TABLE III

Calculated and Experimental T_1 (in eV) and D Values (in cm^{-1}) of Corannulenes and Related Compounds

Compound ^a	Calculated values					Experimental values	
	T_1	D	D_i	D_o	D_r	T_1	D
C0214	2.09	0.077	0.001	0.077	-0.001	2.10 ± 0.01^b	0.084 ± 0.003^c
C0618	2.64	0.098	0.008	0.082	0.008	2.38 ± 0.04^c	0.097^f
C1022	2.17	0.081	0.017	0.053	0.011		
C1224	1.77	0.059	0.006	0.030	0.023		
C1426	2.07	0.079	0.016	0.050	0.013		
C1628	1.48	0.059	0.013	0.024	0.022		
C1830a	2.19	0.089	0.023	0.059	0.007	2.11 ± 0.02^d	0.101 ± 0.006^d
C1830b	1.32	0.053	0.007	0.023	0.023		
1	1.76	0.059					
2	1.44	0.051					

^a Cf. Figure 1. ^b Ref. 15a,b. ^c Ref. 15a,c,d. ^d Ref. 16. ^e Ref. 15,b,e. ^f Ref. 15c,f,g.

values for the few known compounds is good. As expected on reasons discussed above the calculated excitation energies T_1 are higher than the experimental ones. The calculated D of kekulene C1830a is somewhat too low. Here the use of equal bondlengths is not an adequate description of the molecule in the triplet state as will be discussed in a forthcoming paper¹¹. It is striking that an increase or a decrease of T_1 is also accompanied by a corresponding change in D . The same behavior can also be observed with $[4n+2]$ annulenes, cf. Table I and II. This fact was already observed by Brinen and Orloff¹⁷ in a small series of conjugated compounds. However, they did not succeed in finding any explanation except in the case of linear polyacenes. An extended report on this fact will be published in due time¹¹. A planar alternant hydrocarbon with low T_1 will thus also have a low D value. The use of a regression line allows the estimation of D with an uncertainty of only 0.01 cm^{-1} from T_1 .

As stated above D should decrease with increasing size of the molecule. This is, however, only valid in a very general sense, cf. reference 11, there

will be always molecules with much higher or lower D values than expected. For example, $D(C0618) > D(C0214)$ although coronene $C0618$ has 8 carbon atoms more than pyrene $C0214$. The high D value of coronene is due to the fact that it belongs to the point group D_{6h} . In reference 11 it is shown that generally compounds with such a high symmetry will have larger D values than compounds of the same size but with lower a symmetry. The same effect is found in a very impressive way with kekulene $C1830a$, especially if compared with its isomer $C1830b$ which should have a much smaller D value according to our calculation. Here we find a great difference to the annulenes where geometrical isomers do not differ so much in their T_1 and D values.

As we see in Table III we cannot divide corannulenes into two classes according to their T_1 or D values, one with $[4n]$ - and the second with $[4n+2]$ perimeters. For example, $C1224$ and $C1628$ have similar D values as $C1830b$. This contrasts with the magnetic exaltations which have been calculated¹⁸ to be quite different for both types of corannulenes. Unfortunately it was impossible to formulate a benzenoid alternant corannulene with $[4n]$ perimeters without strain belonging to point group D_{6h} due to computational limitations. But we expect that such a corannulene will also show an extraordinary high D value.

In corannulenes we can split the ZFS parameter according to $D = D_o + D_i + D_r$, where $D_{o(i)}$ is the contribution of the outer (inner) perimeter and D_r essentially that of all radial bonds. $D_r = 0$ implies that D is composed entirely of the perimeter values. This is realized only in the case of pyrene $C0214$ where the outer perimeter exclusively makes up D . With all other corannulenes we find $D_r > 0$, i. e. the radial bonds enlarge D . Neglecting all radial bonds corannulenes turn to two concentric annulenes. The triplet state of such a system is identical with that of the outer annulene alone. Therefore, a very weak coupling between both perimeters would result in a T_1 and D very similar to that of the outer annulene, i. e. $D \approx D_o$. As mentioned above this is the case for pyrene $C0214$, however, pyrene in the triplet state is nevertheless no slightly perturbed $[14]$ annulene since then one should get a much higher D , cf. Table II. We can conclude that corannulenes cannot be considered as annulenoid systems in the triplet state as was earlier shown for the groundstate^{6,16,18,19}. Generally we have $D_o > D_i$ which means that both unpaired electrons have a greater probability to be in the outer perimeter than in the inner one. D_o and D_i reflect roughly the changes in D , merely D_i of coronene $C0618$ does not fit in this scheme. Those corannulenes having small D values are characterized by a large D_r , whereas coronene $C0618$, $C1022$, $C1426$, and $C1830a$ exhibit much smaller D_r , i. e. the probability to find the unpaired electrons at both carbon atoms of a radial bond is decreased.

Filling up the hollow in $C1022$ and $C1426$ with 6-rings results in the highly condensed hydrocarbons 1 and 2 whose D values are smaller by $0.02-0.03 \text{ cm}^{-1}$. This corresponds clearly to the enlarged area allowing a wider separation of the two unpaired electrons. This expresses the unique features of corannulenes compared with the usual condensed benzenoid hydrocarbons.

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SAŽETAK

D-parametri cijepanja u nultom polju za makrocikličke sustave

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U okviru pi-elektronskog modela izračunani su tripletni D-parametri cijepanja u nultom polju za $[4n]$ - i $[4n+2]$ -anulene. Ovisnost parametra D o n i stupanj alternacije duljina veza su uspoređeni sa svojstvima temeljnog stanja kao što su npr. magnetske struje u prstenu. Dalje je pokazano da se u tripletnom stanju koralnuli ne mogu smatrati makrocikličkim anulenooidnim sustavima.

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