A Concept to Relate the ZFS Parameter D of Aromatic Hydrocarbons to Molecular and Electronic Structure

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New aspects for the interpretation of the zero field splitting parameter D of the lowest excitet triplet state of polycyclic hydrocarbons are presented. A model connecting the dipole-dipole interaction between the two triplet electrons with Clar's concept of electronic sextets is employed. It follows that even in highly condensed aromatic molecules the probability for the two triplet electrons to be localized on one C_6-ring unit can be relative high.

This concept is outlined taking the experimental D-values of a series of pyrene derivatives as an example.

Aromatic hydrocarbons often are used to study the relations between molecular structure and physical quantities as for instance in the ground state the kinetic constants of chemical reactions [1], susceptibilities [2] and NMR coupling constants [3]. Also properties of the excited state [4, 5] can be related to the structure of aromatic hydrocarbons.

Using the optical detection of magnetic resonance (ODMR) [6] we investigated the lowest excited triplet state T_1 of a number of pyrene derivatives. We looked into the influence of structure and degree of annellation on triplet parameters such as zero field splitting (ZFS), the kinetics of population and depopulation of the individual zero field levels (ZFL's) and the symmetry of the phosphorescence bands [7].

In this notice we shall give a preliminary report of our findings concerning the variation of the D-parameter with structure and degree of annellation.

The molecules can be divided into 4 groups:

1. linear annellation on one side: 1,2-benzopyrene (1,2-BP), 1,2-naphthopyrene (1,2-NP), 1,2-anthracenopyrene (1,2-AP);
2. symmetrical linear annellation on two sides: 1,2;6,7-dibenzopyrene (1,2;6,7-DBP), 1,2;6,7-dinaphthopyrene (1,2;6,7-DNP);
3. unsymmetrical linear annellation on two sides: 1,2;6,7-benzonaphthopyrene (1,2;6,7-BNP), 1,2;6,7-benzoanthracenopyrene (1,2;6,7-BAP);
4. angular annellation: 3,4-benzopyrene (3,4-BP), 1,2;4,5-dibenzopyrene (1,2;4,5-DBP).

The structures are shown in Figure 1.

Samples were prepared from solutions of the molecules in n-alcanes of suitable C-chain length (C_6–C_{12}) yielding quasilinear phosphorescence spectra because of the Shpolskii-effect. Accordingly also the ODMR resonance lines are relatively sharp (1–4 MHz). Practically no dependence of the D-parameters on the C-chain lengths could be observed (e.g. 1,2-BP/n-hexane: $D = 2727{,}0$ MHz; 1,2-BP/n-octane: $D = 2724{,}5$ MHz). Slightly greater changes of D (appr. ± 25 MHz) can be observed for different sites. The results presented here were obtained with samples showing only one site or one site with outstanding intensity. So the interactions between the different molecules and their host matrices are of comparable strength and the influence of the solvent on the D-parameters may be neglected to a very large extent.

The magnetic axis system chosen is included in Figure 1. In the case of the pyrene derivatives with angular annellation the out-of-plane axis is assumed to be the z-axis whereas no assignment of x and y can be given. The hamiltonian for the zerofield splitting then is

$$H_{ss} = D(S_z^2 - 2/3) + E(S_y^2 - S_x^2)$$

with

$$D \propto \langle |(r^2 - 3z^2)/r^5| \rangle .$$

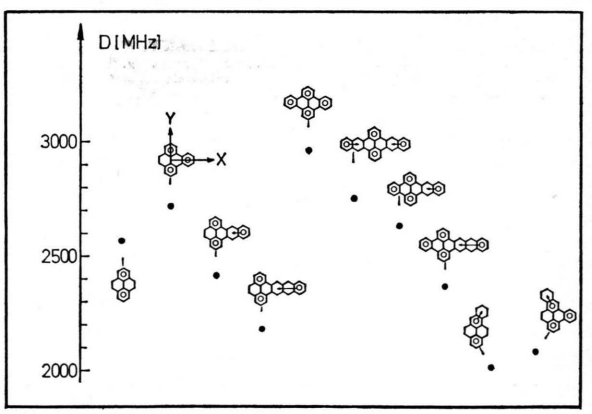

Fig. 1. The zero field splitting parameter D of the lowest excited triplet state of a series of pyrene derivatives. The D-value of pyrene is taken from Ref. [17].

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It is known that for aromatic molecules the out-of-plane level t_z is lowest in energy [8], so for all molecules investigated here $D > 0$.

Figure 1 shows the values of D. It can be seen that D varies systematically within certain groups of molecules. For instance, D decreases with increasing annellation on one side of the pyrene skeleton: from 1,2-BP to 1,2-NP to 1,2-AP (group 1). A similar behaviour can be seen for the molecules of group 2 and group 3. Very small values of D have been found for pyrene derivatives with angular annellation.

Throughout the literature [6, 9] a qualitative model of the dipole-dipole interaction of the two triplet electrons is employed to explain the relative size of D. Because of the greater average separation of the two triplet electrons in greater aromatic molecules with increasing π-electron system D should decrease with the size of the molecules. So the variation of D within each of the groups 1, 2 and 3 as shown above is in agreement with this model. However, the model fails to explain the increase of D upon annellation of a further benzene ring as in the series from pyrene to 1,2-BP to 1,2;6,7-DBP; 1,2-NP to 1,2;6,7-BNP; 1,2-AP to 1,2;6,7-BAP and 3,4-BP to 1,2;4,5-DBP. Since this increase is of the same order of magnitude as the decrease within the groups 1, 2 and 3 the dipole-dipole model cannot be applied with respect only to the size of the π-electron system.

If, however, Clar's concept of the π-electron sextet [10] is taken into account the changes in the size of D can be understood quite easily with the help of the rules formulated below. Clar's concept of the aromatic sextet has been justified quantum mechanically by Polansky and Derflinger [11]. According to their parsorbital-calculations there are localized benzoid regions in polycyclic aromatic hydrocarbons. These localized benzoid C_6 ring units are of strong benezene-like character and can be represented through Clar's concept.

If this concept is applied to our findings it is seen that D increases upon annellation of a further benzene ring if this leads to the formation of another sextet; D decreases if no additional sextet is created. It is obvious that the D-parameter of aromatic hydrocarbons does not depend primarily on the size of the π-system but on the number of localized benzoid structures. Other experimental data [12] show that even polycyclic systems containing up to 13 benzene rings have D-values of up to 3000 MHz if they are of fully benzoid character. That means that in the triplet state too there are localized benzoid structures and that the conjugation of the π-system also is partly localized and does not extend in full strength over the whole molecule. So for the two triplet electrons there is an enhanced probability to be localized on the same benzoid subunit and D will be rather high because of the increased interaction between the two electrons.

Within this concept it is quite clear that a correlation of D with the size of the molecule is only possible if the number of benzoid sextets remains the same. Only then a decrease of D upon an increase of the degree of annellation is expected because the benzoid character of the electronic sextets decreases and the π-conjugation increases (cf. arrows in Fig. 1 and the character orders in [11]).

From the results of the pyrene derivatives presented here it can be seen that a further criterion for the value of D within a series of molecules containing the same number of benzene rings and sextets is given by the molecular symmetry. In conclusion we arrive at the following three rules for the value of the D-parameter:

1. Of two aromatic molecules containing the same number of benzene rings the molecule with the higher number of Clar's electron sextets will exhibit the higher value of D.

   Examples: 1,2-NP—1,2;6,7-DBP
   1,2-AP—1,2;6,7-BNP
   3,4-BP—1,2-BP
   1,2;4,5-DBP—1,2;6,7-DBP.

2. Of two aromatic molecules containing the same number of benzene rings and of Clar's electron sextets the molecule with higher symmetry will exhibit the higher value of D.

   Examples: 1,2;6,7-BAP—1,2;6,7-DNP
   1,2;4,5-DBP—1,2-NP.

3. Of two aromatic molecules belonging to the same symmetry group and forming the same number of Clar's electron sextets the molecule containing the lower number of benzene rings will exhibit the higher value of D.

   Examples: 1,2-AP—1,2-NP—1,2-BP
   1,2;6,7-DNP—1,2;6,7-DBP
   1,2;6,7-BAP—1,2;6,7-BNP.

Fully benzoid systems of high symmetry will show the highest value of D. These rules are valid within each series of derivatives e.g. pyrenes, coronenes [12, 13], acenes, substituted anthracenes [14]. Based on the accessible data work in attempt to connect the findings in the different series quantitatively is done at the moment. Further, calculations are performed to correlate D with the character orders of the triplet state [15] because for the D-parameter of polycyclic hydrocarbons the benzoid character orders of the triplet state are of physical importance.

An interpretation of the E-parameter of the pyrene derivates within the framework presented here is also possible.

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