

Correlations between the Ground State and the Triplet State Character Orders of Benzenoid Hydrocarbons

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The relative localization of the π -conjugation of benzenoid hydrocarbons in the ground state S_0 and the lowest excited triplet state T_1 is described by means of character orders. For molecules with the same number of electron sextets a linear correlation could be found between the mean character orders of S_0 and T_1 indicating the similarities in the electron distribution of these states. The relevance of this similarity for an earlier explanation of the zero-field splitting in T_1 is given.

Recently we have developed a concept [1] to explain the variation of the zero-field splitting (ZFS) parameters D and E of the lowest excited triplet state T_1 with the structure of aromatic hydrocarbons. As model compounds a series of systematically selected pyrene derivatives were investigated by means of ODMR methods. The variation of the experimentally determined ZFS-parameters could be correlated with criteria describing the local benzene likeness of single C_6 -rings in the molecule. Such criteria can be obtained on a MO basis using e.g. the character orders (COs) of Polansky and Derflinger [2]. Since the ZFS parameters are given as the expectation value of the dipole-dipole operator with the triplet wavefunction [1] it is desirable to use COs of the triplet state [3]. However in [1] COs of the ground state were used for simplicity and in order to be consistent with the graph theoretical indices [4] which were applied too. So far these latter criteria are not defined for excited states.

In Ref. [1] it was already mentioned that there are reasons which justify the application of ground state COs instead of those of the triplet state. Because this is a question of general interest we want to supplement our earlier approaches in the following sections showing explicitly how COs of ground and triplet states are correlated.

According to Polansky [3] the CO q_L of the subunit L is defined by the equation

$$q_L = -1 + \frac{1}{N} \sum_r \sum_s (p_{rs}^L + u_{rs} u_{rs}^L), \quad (1)$$

where p_{rs} and p_{rs}^L are the bond orders of the molecule and the subunit L , respectively, N is a normalisation factor, the summation is taken over that part of the molecule where the subunit is located, and u_{rs} and u_{rs}^L are given for the molecule and the subunit L as $u_{rs} = p_{rs}^\alpha - p_{rs}^\beta$. One obtains p_{rs}^α and p_{rs}^β by summing over MOs with only α or β spins, respectively, so that $u_{rs} = 0$ for the ground state and $u_{rs} \neq 0$ for the excited states.

Equation (1) offers the possibility to calculate different kinds of COs. We are interested in the benzenoid COs 0q of the ground state and 3q of the triplet state, respectively. These indicate to what degree the ground state or the triplet state of benzene is represented in a special C_6 ring unit of the molecule, which itself is in the ground state or the triplet state, respectively. Within a semiempirical π -theory [5] values of 0q and 3q were obtained for the aromatic hydrocarbons given in ref. [1] and are summarized in Figure 1. A comparison between the COs 0q and 3q of the equivalent C_6 -rings shows the following:

- 1) The triplet state COs 3q have all higher values than the ground state COs 0q .
- 2) The variations of the COs 3q and 0q within one molecule are very similar, however small deviations occur between the order in which the COs from the highest to the lowest values are distributed over the C_6 -rings of the molecules.
- 3) The relative variations of the COs *from molecule to molecule* — as discussed in Ref. [1] — are the

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same for the ground state and the triplet state. So for example in the ground state the COs ${}^0\bar{\rho}$ are nearly identical in the long acene rest if one compares 1,2-benzo-pyrene with 1,2;6,7-dibenzopyrene, naphtho-(2',3':1,2)-pyrene with 1,2-benzo-naphtho-(2',3':6,7)-pyrene and anthraceno-(2',3':1,2)-pyrene with 1,2-benzo-anthraceno-(2',3':6,7)-pyrene. The same is true in the triplet state for the COs ${}^3\bar{\rho}$. Other examples can be easily found in Figure 1.

4) The relative localisation and delocalisation of the conjugation in the π -electron system of the benzenoid hydrocarbons, indicated by the variations of the COs [1], are very similar for the ground state and the triplet state.

In Fig. 1 the mean COs $\bar{\rho}$ are also given as numbers, standing below each molecule. As an average value they indicate the overall aromaticity [1, 4] of a molecule. Because of points 1) to 4) in the foregoing discussion it is not surprising that the mean COs of the triplet state and the ground state can be quantitatively related. For molecules with the same number of electron sextets [6] close correlations of the form

$${}^3\bar{\rho} = a {}^0\bar{\rho} + b \quad (2)$$

are found. The value for a and b and the correlation coefficients r are given in Table 1. The values of r indicate that the relative variations of the overall

Table 1. The data for the correlation ${}^3\bar{\rho} = a {}^0\bar{\rho} + b$.

Molecules ^a	a	b	r
1,2-BP; 1,2-NP; 1,2-AP	1.003	84.58	0.995
1,2; 6,7-DBP; 1,2; 6,7-BNP; 1,2; 6,7-BAP	0.534	478.5	0.999
N, A, T	0.641	404.1	0.996
B, N, A, T	0.302	702.5	0.953

^a for the abbreviation see Figure 1.

aromaticities of the molecules in the ground state and the triplet state are very similar.

The good correlation between ${}^3\bar{\rho}$ and ${}^0\bar{\rho}$ leads also to an accordingly good correlation between the ZFS parameters D and E and the ${}^3\bar{\rho}$ -values, as expected. The data for this correlation can easily be obtained from the data in Table 1 and Fig. 1 as well as the D and E values from [1]. Such a correlation is shown in Figure 2.

Only for the acenes some small difficulties arise. If benzene is included in the correlation of (2) the correlation coefficient is smaller than without benzene. The same is true for the correlations between the ZFS parameters D and E and the mean triplet COs ${}^3\bar{\rho}$ of the acenes, however the correlation with the ground state COs ${}^0\bar{\rho}$ is excellent. This is a puzzling behaviour and may have to do with the in principal much higher values of ${}^3\bar{\rho}$ compared ${}^0\bar{\rho}$ but

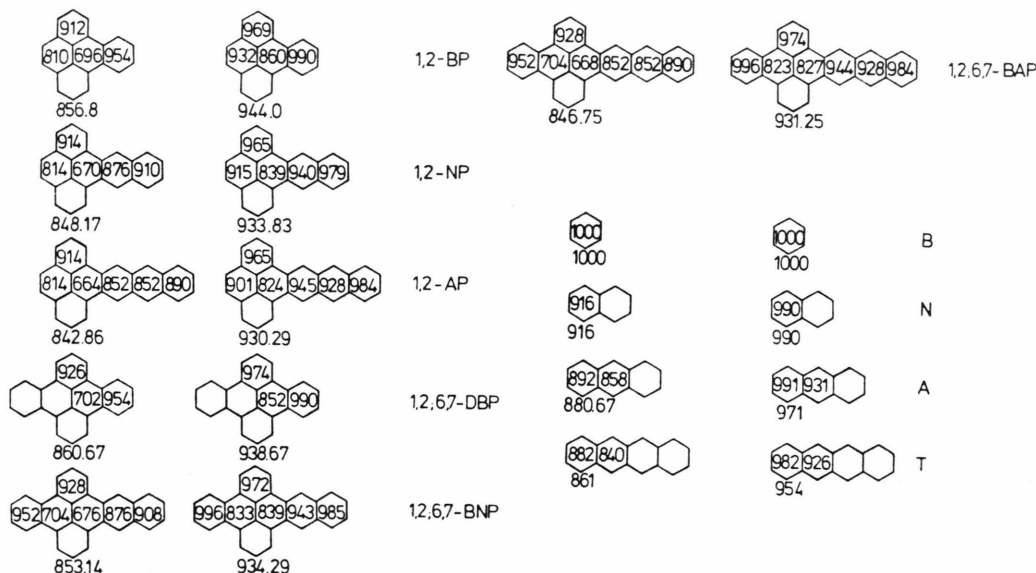


Fig. 1. The benzenoid character orders of the ground state (left molecule of each pair) and the triplet state (right molecule of each pair). The abbreviations of the names of the molecules are given on the right side of each pair.

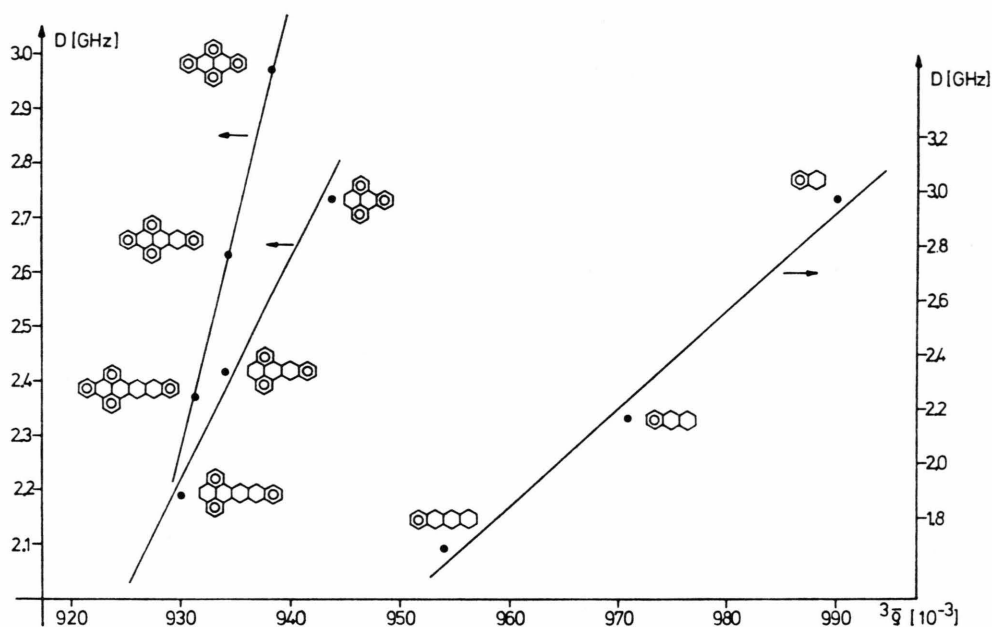


Fig. 2. The linear correlation between the zero-field splitting parameter D and the mean triplet character order ${}^3\bar{q}$. The correlation coefficients are given by $r > 0.99$.

the same value of both for benzene. So the drop of ${}^3\bar{q}$ between the first two members in the series, benzene and naphthalene, is small in the triplet state but large in the ground state.

In summary it can be stated for the molecules investigated that not the absolute but the relative electron distributions are very similar between the ground state and the triplet state. This may be extended to other alternant aromatic hydrocarbons. It is interesting that such similarities can not be

obtained if one compares other types of COs which indicate to what degree the ground state of benzene is represented in a special C_6 ring unit of the molecule which itself is in the lowest excited singlet or triplet state, respectively.

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