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# THE ZERO-FIELD SPLITTING PARAMETER D OF THE TRIPLET STATE $T_1$ OF BENZENOID HYDROCARBONS DESCRIBED IN TERMS OF BASIC MOLECULAR SUBUNITS

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**Abstract**—The zero-field splitting parameter D has been studied in dependence of the structure and topology of benzenoid hydrocarbons. A recent explanation in terms of localized benzenoid indices could be extended to larger molecular subunits. These have to be weighted according to the number of contributing Kekulé structures. Four rules for the determination of D could be formulated. For all known D-values of benzenoid hydrocarbons (26 molecules) the theoretical D-values calculated according to the rules are in excellent agreement with the experimental data. With the method described the D-values of a great number of mulecules can be determined easily and accurately from the D-values of only few basic types of molecules.

## 1. THE ZFS-PARAMETER D AND THE KEKULÉ STRUCTURES OF BENZENOID HYDROCARBONS

The zero-field splitting (ZFS) of the triplet state is pictured schematically in Fig. 1. It is a characteristic of the triplet state and depends distinctly on the size and topology of benzenoid hydrocarbons. This dependence follows from the Hamiltonian:[1]

$$H_{ss} = D(S_z{}^2 - 2/3) + E(S_x{}^2 - S_y{}^2) \qquad (1)$$

for the magnetic dipolar interaction of the two triplet electrons. As can be seen from eqn (1) and Fig. 1, the magnitude of the ZFS is given by the ZFS-parameters D and E, which within the restricted Hartree–Fock approximation and with neglect of the exchange part are given as follows

$$D = 3/4g^2\beta^2 \left\langle {}^3\psi \left| \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5} \right| {}^3\psi \right\rangle \qquad (2)$$

$$E = 3/4g^2\beta^2 \left\langle {}^3\psi \left| \frac{y_{ij}^2 - x_{ij}^2}{r_{ij}^5} \right| {}^3\psi \right\rangle. \qquad (3)$$

As the indices i and j mark the two unpaired triplet electrons D and E depend on the coordinates of the two triplet electrons and on their distance from each other $r_{ij}$.

Recently[2] the ZFS parameters of a series of systematically selected pyrene derivatives could be interpreted in terms of increasing or decreasing benzene-like character of single $C_6$-ring units in the benzenoid molecules. Although due to these results the variation of the ZFS-parameters with molecular structure could be described in a simple and clear manner within *certain* series of benzenoid hydrocarbons, e.g. pyrenes, it was still not possible to give a more general and quantitative description for *all* benzenoid hydrocarbons. Since the ZFS and especially the D-parameter are very characteristic properties of the triplet state[1] describing localization or delocalization of the $\pi$-conjugation system[2] it is highly desirable to have a more general concept which can describe all D-values measured so far and further allow predictions of the D-values of other benzenoid hydrocarbons.

As the former models[2] in principle were based on molecule-in-molecule calculations taking benzene as a subunit the attempt of building the molecule from larger subunits seems promising. Obviously in doing so principles have to be observed mainly concerning the subunits making up the molecule and the weighting of these subunits. If the following four rules are observed one finds excellent agreement between the D-values calculated according to these rules and those determined experimentally. This applies to all known D-values except those of the few compounds called fully benzenoid by Clar.[3]

*Rule* 1. In building the molecule only such subunits must be used whose Kekulé structures are found in the Kekulé structure of the molecule.

*Rule* 2. The subunits must overlap in one $C_6$-ring. No isolated subunit must join a neighbouring one. Together the subunits must conform to the overall form of the molecule.

*Rule* 3. The number of Clar's sextets in the molecule must be equal to the sum of the sextets of all subunits.

*Rule* 4. The contribution of the subunits to the molecule's D-value is weighted with the number of its own possible Kekulé structures $K_L$. The molecule's D-value then is equal to the sum of the weighted $D_L$-values of the subunits L divided by the sum of the possible Kekulé structures in the subunits L:

$$D = \frac{\sum\limits_L D_L \cdot K_L}{\sum\limits_L K_L} \qquad (4)$$

The application of the rules shall be demonstrated for several examples of the series of pyrene derivatives.

1,2-Benzopyrene (1,2-BPy) can be combined of pyrene (Py) and naphthalene (N) according to rules 1,2, and 3 (see Fig. 3). As pyrene has 6 Kekulé structures and naphthalene has 3 the D-value of 1,2-benzopyrene is calculated according to eqn (4) with the D-values of pyrene (D = 2.572 GHz) and naphthalene (D = 2.980) as D = 2.708 GHz. The experimental value is D = 2.724 GHz, so the error is 0.6%.

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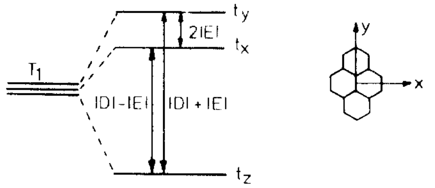


Fig. 1. The zero-field splitting of the lowest excited triplet state $T_1$ and the magnetic axis system for a representative molecule.

In the same manner naphtho-(2′,3′; 1,2)-pyrene (1,2 NPy) and anthraceno-(2′,3′; 1,2)-pyrene (1,2-APy) can be put together of pyrene ($D = 2.572$ GHz), anthracene (A) ($D = 2.153$ GHz) and tetracene (T) ($D = 1.708$ GHz) respectively with weights of 6 and 4 or 6 and 5 respectively. The resulting D-values are $D = 2.404$ GHz and $D = 2.179$ GHz respectively. The corresponding experimental D-values are $D = 2.410$ GHz and $D = 2.179$ GHz respectively. The error is less than 0.2%. In analogy to the application of the four rules demonstrated for the three examples above the D-values of further benzenoid hydrocarbons were calculated. They are shown in Table 1.

Table 1 summarizes the results for all benzenoid hydrocarbons for which the D-values could be found in the literature[1,4–9] or were obtained from our own experiments.[2,10–13] The D-parameters of the molecules 1,2;7,8-dibenzochrysene (1,2;7,8-DBCh), tetrabenzotetracene (TBT), 1,2;3,4;5,6-tribenzocoronene (1,2;3,4;5,6-TBC), 1,2-benzo-dinaphtho-(1″,2″: 3,4); (1‴.2‴: 9.10)-pyrene (1,2;3,4;9,10-BDNPy) and tetrapheno-(6,′5′: 5,6)-tetraphene (TphTph) in Table 1 are published for the first time. They were determined with the ODMR-apparatus described in Refs. [11, 14].

For each molecule in Table 1 a number of ways is indicated by which the molecule can be put together according to rules 1,2, and 3. The D-value according to eqn (4) is shown as $D_{th}$ for each possibility. This value can be compared with the experimental D-value listed in the next column. The solvent matrix for the particular measurement and the reference are given in the following columns. The difference $\Delta D$ between the theoretical and experimental values listed in the last column of Table 1 are extraordinarily small. For most of the cases they are less than 2%, and for all cases less than 5%. Figure 2 gives a plot of the theoretical D-values vs the experimental D-values with $r = 0.994$. So the error margin for the theoretical value is within the margin which can be caused by the solvent. This is an extremely good result and supports the concept formulated here.

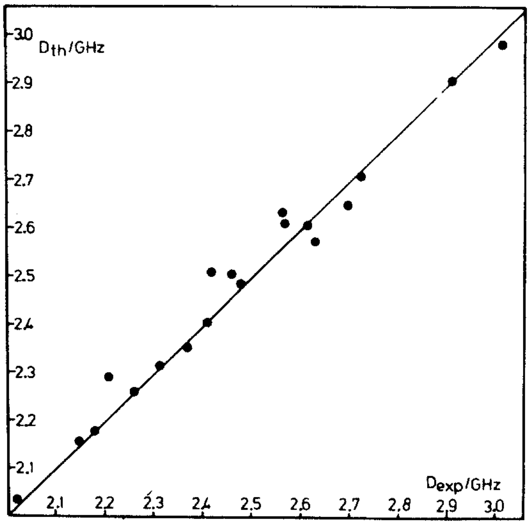


Fig. 2. $D_{th}$ vs $D_{exp}$ according to the data of Table 1. $r = 0.994$.

## 2. DISCUSSION OF THE RULES FOR THE CALCULATION OF D

Figure 3 shows the 11 Kekulé structures of 1,2-benzopyrene. It can easily be seen that the Kekulé structures of pyrene or naphthalene occur 6 or 3 times in the Kekulé strucures of 1,2-benzopyrene. These are exactly the numbers of Kekulé structures possible in pyrene or naphthalene themselves and are therefore the weighting factors for these molecules in eqn (4). An analogous situation is found in the case of naphtho(2′,3′; 1,2)-pyrene with 16 Kekulé structures and anthraceno-(2′,3′; 1,2)-pyrene with 21 Kekulé structures.

These examples illustrate the analogy to Pauling's bond order.[15,16] In this description one counts the relative number of double-bonds between two atoms for all Kekulé structures possible and so obtains a measure of the double-bond character. In a similar manner the number of the Kekulé structures in 1,2-benzopyrene is a measure of how much pyrene contributes to 1,2-benzopyrene. So this is in principle an extension of Pauling's bond order. It therefore seems reasonable to weight the D-value of pyrene with a factor of 6 and that of naphthalene with a factor of 3 in the calculation of the D-value of 1,2-benzopyrene according to eqn (4). If this weighting in eqn (4) is taken as a measure of as to what degree a particular subunit contributes to the whole molecule rule 4 becomes intelligible.

Besides the extension of Pauling's bond order the character orders according to Polansky *et al.*[17] are an alternative possibility to describe the contribution of a particular subunit to the whole molecule. Since the concept of Pauling's bond order is a typical element of resonance theory[15] and the character orders are calculated on a MO basis it is of great interest whether both theories give the same result. Therefore the character orders $\rho_L$ of those subunits which were considered for the pyrene molecules in Tables 1 were calculated for the pyrene derivatives by means of a Hückel calculation. (Because of some advantages only the ground state character orders were calculated instead of those of the triplet state. However, it was shown in Ref. [18] that both correlate closely for alternant hydrocarbons and can be interchanged in applications as in eqn (4) where only relative values are important.) Using these character orders as weighting factors instead of $K_L$ in eqn (4) the D-values of the pyrene derivatives were obtained as listed in Table 2, together with the D-values calculated according to eqn (4) where $K_L$ was taken and those determined experimentally. The good

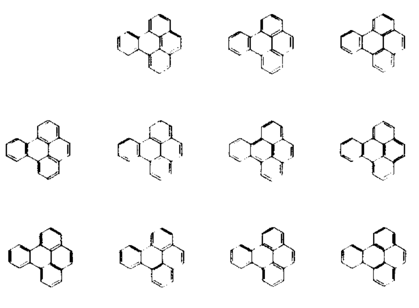


Fig. 3. The Kekulé structures of 1,2-benzopyrene.

Table 1. Experimental D-values and those calculated according to eqn (4) using the subunits in column 2. D-values given in GHz. The last column gives the relative differences. (a) Explanation of the abbreviations of the matrices: $N_{d8}$ = perdeuteronaphthalene; Fl = fluorene, MTHF = methylthetrahydrofurane; PMMA = polymethacrylacidm-ethylester; n-12 = dodecane; n-10 = n-decane; n-9 = n-nonane; n-8 = n-octane; n-7 = n-heptane. (b) This value was extrapolated according to Ref. 2. (c) This value was calculated from 1,2-benzocoronene with eqn (4)

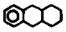
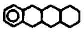
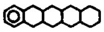
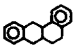
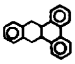
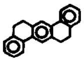
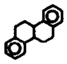
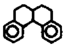
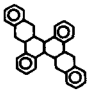
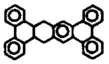
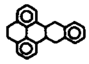
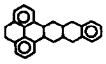
| Molecule | Subunits | $D_{th}$ | $D_{exp}$ | Matrix (a) | Ref. | ΔD % |
|---|---|---|---|---|---|---|
| <br>N | | | 2.980 | $N_{d8}$ | 4 | |
| <br>A | | | 2.153 | Fl | 4 | |
| <br>T | | | 1.708 | n-10 | 5 | |
| <br>P | | | 1.382 (b) | | 2 | |
| <br>Ph | 3N + 3N | 2.980 | 3.013 | Fl | 6 | 1.1 |
| <br>1,2-BA | 4A + 3N | 2.507 | 2.418 | n-7 | 5 | 3.7 |
| <br>1,2;3,4-DBA | 4A + 3N + 3N | 2.649 | 2.565 | n-8 | 5 | 3.2 |
| | 7(1,2-BA) + 3N | 2.587 | | | | 0.8 |
| | 5Ph + 4A | 2.631 | | | | 2.6 |
| <br>1,2;5,6-DBA | 4A + 3N + 3N | 2.649 | 2.698 | MTHF | 7 | 1.8 |
| | 7(1,2-BA) + 3N | 2.587 | | | | 4.2 |
| <br>Ch | | | 2.848 | n-8 | | |
| <br>3,4-BPh | | | 2.774 | n-8 | 13 | |
| <br>1,2;7,8-DBCh | 8Ch + 3N + 3N | 2.905 | 2.909 | n-8 | | 0.1 |
| | 8(3,4-BPh) + 3N + 3N | 2.862 | | | | 1.6 |
| <br>TphTph | 8Ch + 4A + 4A | 2.501 | 2.459 | PMMA | | 1.7 |
| <br>TBT | 5T + 3N + 3N + 3N + 3N | 2.606 | 2.614 | n-8 | | 0.3 |
| <br>Py | | | 2.572 | n-7<br>MTHF | 2<br>8 | |
| <br>1,2-BPy | 6Py + 3N | 2.708 | 2.724 | n-8 | 2 | 0.6 |
| <br>1,2-NPy, | 6Py + 4A | 2.404 | 2.410 | n-8 | 2 | 0.2 |
| <br>1,2-APy | 6Py + 5T | 2.179 | 2.179 | n-10 | 2 | 0.0 |

Table 1. (*Contd*).

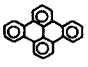
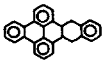
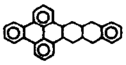
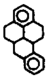
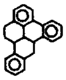
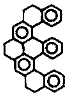
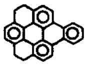
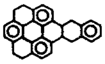
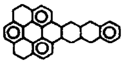
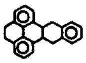
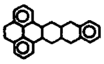
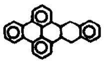
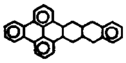
| Molecule | Subunits | $D_{th}$ | $D_{exp}$ | Matrix (a) | Ref. | ΔD % |
|---|---|---|---|---|---|---|
| <br>1,2;6,7-DBPy | 6Py + 3N + 3N | 2.776 | 2.969 | n-10 | 2 | 6.6 |
| | 11(1,2-BPy) + 3N | 2.779 | | | | 6.4 |
| <br>1,2;6,7-BNPy | 6Py + 4A + 3N | 2.537 | 2.630 | n-10 | 2 | 3.5 |
| | 11(1,2-BPy) + 4A | 2.572 | | | | 2.2 |
| | 16(1,2-NPy) + 3N | 2.500 | | | | 4.9 |
| <br>1,2;6,7-BAPy | 6Py + 5T + 3N | 2.351 | 2.371 | n-12 | 2 | 0.8 |
| | 11(1,2-BPy) + 5T | 2.407 | | | | 1.5 |
| | 21(1,2-APy) + 3N | 2.279 | | | | 3.9 |
| <br>3,4-BPy | | | 2.022 | n-8<br>n-8 | 2<br>9 | |
| <br>(1,2;4,5)-DBPy | 9(3,4-BPy) + 3N | 2.262 | 2.262 | n-10 | 2 | 0.0 |
| <br>1,2;3,4;9,10-BDNPy | | | 2.404 | PMMA | | |
| <br>1,2-BC | 14(1,12-BPe) + 4A | 2.319 | 2.349/2.277 | n-9 | 11 | |
| | 9Pe + 4A + 3N | 2.313 | | | | |
| <br>1,2-NC | 14(1,12-BPe) + 5T | 2.193 | 2.161/2.136 | n-10 | 11 | 3.1 |
| | 9Pe + 5T + 3N | 2.154 | | | | 0.3 |
| <br>1,2-AC | 14(1,12-BPe) + 6P | 2.071 | 2.020 (b) | | | 2.5 |
| | 9Pe + 6P + 3N | 2.038 | | | | 0.9 |
| <br>1,12-BPe | 9Pe + 3N | 2.366 | | | | |
| <br>Pe | | 2.162 (c) | | | | |
| <br>1,2;5,6-DBC | 34(1,2-BC) + 3N | 2.400/2.333 | 2.493/2.458 | n-8 | 11 | 3.7 |
| | 11(1,2-BPy) + 4A + 4A | 2.484 | | | | 0.3 |
| | 6Py + 4A + 4A + 3N | 2.447 | | | | 1.7 |
| | 9Pe + 4A + 3N + 3N | 2.418 | | | | 1.6 |
| | 14(1,12BP) + 4A + 3N | 2.413 | | | | 1.6 |
| <br>1,2;3,4;5,6-TBC | 16(1,2-NPy) + 4A + 4A | 2.324 | 2.207 | n-8 | | 5.1 |
| | 6Py + 4A + 4A + 4A | 2.293 | | | | 3.9 |
| | 5T + 4A + 4A + 3N + 3N | 2.297 | | | | 4.0 |

Table 2. D-values in GHz calculated according to eqn (4) with weightings $\rho_L$ and $K_L$. The character orders were calculated for the subunits indicated in parenthesis. The last column gives the experimental D-values

| Molecule | Character orders $\rho_L$ of the subunits | $D_{th}$ according to eq. (4) weighting with | | $D_{exp}$ |
|---|---|---|---|---|
| | | $\rho_L$ | $K_L$ | |
| <br>1,2-BPy | (Py) = 0.960<br>(N) = 0.878 | 2.767 | 2.708 | 2.724 |
| <br>1,2-NPy | (Py) = 0.950<br>(A) = 0.910 | 2.367 | 2.404 | 2.401 |
| <br>1,2-APy | (Py) = 0.947<br>(T) = 0.929 | 2.144 | 2.179 | 2.179 |
| <br>1,2;6,7-DBPy | (Py) = 0.920<br>(N) = 0.879 | 2.771 | 2.776 | 2.969 |
| <br>1,2;6,7-BNPy | (Py) = 0.910<br>(A) = 0.911<br>(N) = 0.880 | 2.564 | 2.537 | 2.630 |
| | (1.2-BPy)=0.960<br>(A) = 0.911 | 2.446 | 2.572 | |
| | (1,2-NPy)=0.973<br>(N) = 0.880 | 2.681 | 2.500 | |
| <br>1,2;6,7-BAPy | (Py) = 0.907<br>(T) = 0.930<br>(N) = 0.880 | 2.408 | 2.351 | 2.371 |
| | (1.2-BPy)=0.958<br>(T) = 0.930 | 2.224 | 2.407 | |
| | (1.2-APy)=0.977<br>(N) = 0.880 | 2.559 | 2.279 | |
| <br>1.2;4,5-DBPy | (3.4-BPy)=0.967<br>(N) = 0.867 | 2.475 | 2.262 | 2.262 |

agreement of the D-values in Table 2 is very satisfying. This is another support for the concept developed here. The result can be understood because of the great similarities between the resonance theory and the more profound MO theory as has already been pointed out by Longuet-Higgins[19] and Dewar.[20] So for instance, the bond orders of Pauling[16] and Coulson[21] correlate closely[22] whereas the latter form the basis for the character orders of Polansky *et al.*[17]

At this point it is necessary to point out an aspect important for the application of eqn (4) in the case of larger benzenoid hydrocarbons. So far we have said that the Kekulé forms of the subunits pyrene, naphthalene, anthracene and tetracene do occur in just that number in the Kekulé forms of 1,2-benzopyrene, naphtho-(2′,3′; 1,2)-pyrene, and anthraceno-(2′,3′; 1,2)-pyrene in which they do possess Kekulé structures of their own. However, a number of more complex benzenoid hydrocarbons contain some subunits in integer multiples of the number of Kekulé forms possible in these subunits themselves. This can be seen if the Kekulé forms of these hydrocarbons are sketched.

A general formula for $K_{L(M)}$, i.e. the number how often the Kekulé structures of the chosen subunit L occur in the $K_M$ Kekulé structures of the molecule M can be obtained if the molecule M is broken down into the subunit L and a residue R which have $K_L$ and $K_R$ Kekulé forms respectively. For instance, in the case of tetrabenzotetracene (TBT), naphthalene (N) may be chosen as the subunit L with $K_L = 3$ Kekulé structures leaving a residue R consisting of 6 localized double bonds and 6 other ones forming the 4 Kekulé structures of diphenyl, therefore $K_R = 4$. As the Kekulé strucures in L and R are independent from each other for each Kekulé structure of R the whole set of the $K_L$ Kekulé structures of L is found in the Kekulé structure of the molecule M. Therefore we have

$$K_{L(M)} = K_L \cdot K_R. \quad (5)$$

Accordingly for each naphthalene branch the Kekulé structures of naphthalene are found $K_{L(M)} = 3 \times 4 = 12$ times in the Kekulé forms of tetrabenzotetracene.

If it is accepted that, as has been outlined above, the weighting of the D-values of the subunits has to be done according to the extended concept of Pauling's bond order then for tetrabenzotetracene integer multiples of the highest possible number of Kekulé forms in the subunits might have to be considered. The D-values resulting from such a procedure is D = 2.860 GHz. Of course, such a procedure is in contradiction to rule 4 and eqn (4) which demand that the weighting of the subunits corresponds to the number of its own Kekulé forms possible and not to multiples thereof. According to eqn (4) one obtains D = 2.606 GHz. As the experimental value is D = 2.614 GHz obviously eqn (4) gives the correct value. By realizing eqn (5) this becomes clear. As the subunit L and its residue R do not overlap in view of rule 2, R has no meaning for eqn (4); hence $K_R > 1$ should be insignificant too, and consequently $K_L$ has to be used in eqn (4) and not $K_{L(M)}$.

These results, however, which underline the correctness of eqn (4), lead to a partial restriction of the explanation given for eqn (4) in terms of the extension of Pauling's bond order. So this explanation only applies to simpler benzenoid hydrocarbons not containing multiples of the number of possible Kekulé forms of a subunit. For larger benzenoid hydrocarbons, the situation is more complex so that a simple explanation is not possible.

### 3. CONSEQUENCES FOR THE APPLICATION OF RULES 1–4

As the agreement between the experimental D-values of benzenoid hydrocarbons and those calculated according to the rules 1–4 is exceptionally good (see Fig. 2) we assume that by means of these rules also the D-values of further benzenoid hydrocarbons can be obtained quite well. For the first time this would give the possibility to determine the D-values of a great number of molecules on the basis of few and easy to apply rules with great accuracy. Further, at least in the case of simpler benzenoid hydrocarbons, these rules allow an understanding of the variation of D with the structure of benzenoid hydrocarbons on the basis of the extension of Pauling's bond order.

For the calculation of D-values according to rules 1–4 of course the experimental D-values of a certain number of molecules are needed. Of these we term those molecules "basic types" which cannot be put together from further benzenoid subunits according to rules 1, 2 , and 3. As can be seen from Table 1 basic types occurring very often are the polyacenes. The knowledge of their D-values is a prerequisite for the application of rules 1–4. The D-values of the polyacenes[4,5,23] benzene to tetracene are well known, but those of the higher polyacenes could not be determined experimentally, because of their short triplet lifetime and their chemical instability. The simplest and best way to obtain the D-values of the higher acenes is to extrapolate them by means of a correlation as we have shown.[2]

Another way to obtain the D-values of basic types is to calculate them from those of other molecules determined experimentally. This possibility is of particular value if the basic types themselves cannot be measured. Perylene (Pe) is given as an example; for perylene again the desactivation of the triplet state is too fast for the experimental determination of the D-parameter. So in order to obtain the D-value of perylene one determines D of, e.g. 1,2-benzocoronene (1,2-BC). This molecule has a relatively long lifetime and strong phosphorescence; so it is well suited for measurement. As 1,2-benzocoronene according to rules 1,2, and 3 contains perylene by rewriting of eqn (4) D = 2.162 GHz is obtained fo perylene. Further basic types of molecules can easily be found; they are for instance pyrene, 3,4-benzopyrene, chrysene, 3,4-benzophenanthrene, the helicenes, anthanthrene and others. Partly, these have been investigated experimentally; the D-values of the remaining molecules can partly be derived from other available D-values in the manner described.

It should be credited to the principles established here, if from now on only the D-values of few especially selected benzenoid hydrocarbons will be determined which belong to the group of basic types or allow conclusions with respect to such. In this way very few measurements will yield a great number of new data.

Figure 4 shows the D-values of a great number of naphthalene, anthracene- and tetracene derivatives. Most of these D-values have been calculated from basic types of the polyacenes naphthalene to tetracene, chrysene and 3,4-benzophenanthrene, respectively. Experimental values available are given in parentheses. For the fully benzenoid compounds triphenylene and tetrabenzoanthracene no D-values are given because they do not belong

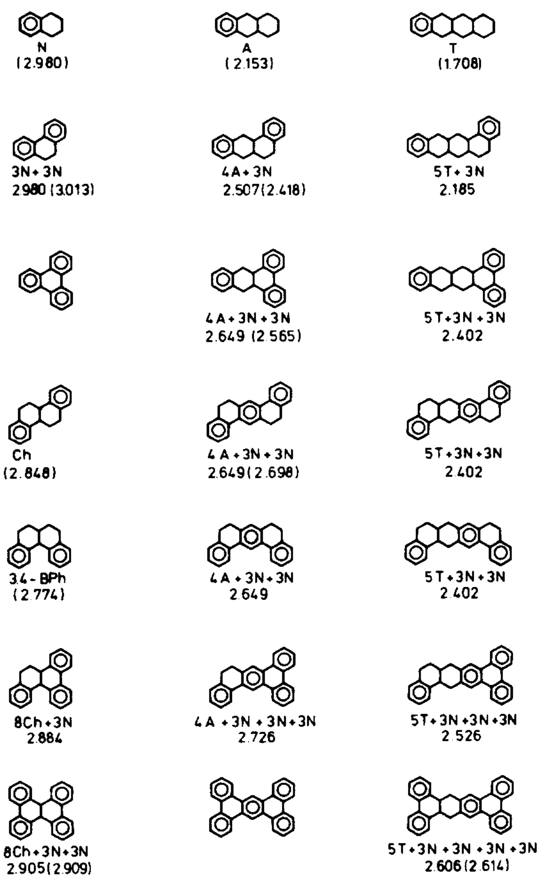


Fig. 4. The D-values of naphthalene-, anthracene- and tetracene derivatives as calculated from the subunits indicated. Experimental D-values given in parentheses.

to the class of molecules discussed here. Figure 4 demonstrates the usefulness of rules 1–4 very clearly.

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