Optical and ODMR Investigations of the Lowest Excited Triplet State of Dinaphtho-(2'.3':1.2); (2''.3'':6.7)-pyrene

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Dedicated to Prof. Dr. G.-M. Schweb on his 80th birthday

On the basis of the phosphorescence spectrum of dinaphtho-(2'.3':1.2); (2''.3'':6.7)-pyrene in n-dodecane (Shpolskii matrix) at \(T = 1.3\) K a site and vibrational analysis was performed. With the help of ODMR measurements the symmetries of the vibrational bands were determined. In this way for most of the normal modes an assignment of the type of vibration became feasible. Because of their different zero-field splittings (ZFS) five sites could be identified. The signs of the ZFS parameters as well as the kinetic rate constants of population and depopulation of the zero-field levels (ZFL) of \(T_1\) were determined. Like the ZFS the kinetic rate constants too were different for each site reflecting different interaction of the molecules with the host matrix. Radiative and radiationless processes are discussed in terms of spin-orbit coupling (SOC).

1. Introduction

Aromatic hydrocarbons often serve as model systems for photophysical processes [1]. Of particular interest are the spin-forbidden transitions between the singlet system and the zero-field levels (ZFL's) of the lowest excited state \(T_1\). The magnetic dipole-dipole-interaction of the two unpaired triplet electrons causes the splitting of the state \(T_1\) into the three ZFL's in the absence of an external magnetic field. This zero-field-splitting (ZFS) is of the order of 0.1 cm\(^{-1}\)—0.01 cm\(^{-1}\).

By means of the Optical Detection of Magnetic Resonance (ODMR) technique [2] the ZFS as well as the kinetics of the ZFL's can be observed quite conveniently. This method combines the high sensivity of optical detection with the good selectivity of ESR. Further it allows a relatively detailed interpretation of the phosphorescence spectra.

We intend to apply the wide scope of the ODMR technique to investigate a number of aromatic molecules containing pyrene as a common basic structure and showing different degrees of annelation. Varying numbers of benzene rings are condensed in differing positions of the pyrene skeleton [3]. In this way the influence of structure and degree of annelation on the ZFS and the dynamics of the ZFL's of \(T_1\) shall be studied. The triplet state of a few pure aromatic molecules has been investigated by ODMR [4—6]. However, their number is small as compared to hetero- and substituted aromatic molecules [2] and the selection has not been very systematic. It seems promising therefore, to engage in such an investigation programme which — as outlined above — should yield information on the influence of structure and degree of annelation on triplet parameters by taking a series of pyrene derivatives as an example.

In this communication we shall present the first results for a typical representative of this class of molecules, the dinaphtho-(2'.3':1.2); (2''.3'':6.7)-pyrene (DNP).

2. Experimental

2.1. Apparatus

The ODMR apparatus has been described before [6]. With it the phosphorescence spectrum at 1.3 K could be recorded. Weak phosphorescence and overlap of intense fluorescence necessitated the use of a light chopper in the excitation path. The chopping frequency was 800 Hz. The 313 nm Hg-line was selected for excitation. The bandwidth of the emission monochromator was adjusted to 1 cm\(^{-1}\).

2.2. Material

The pure DNP [3] was dissolved in highly pure n-dodecane serving as a Shpolskii matrix. Concentrations were \(10^{-4}\) mole/l or less. The samples were degassed and filled into quartz vials which were sealed off under vacuum. Luminescence spectra did not change during the course of the measurements indicating the photostability of the DNP-molecule.
3. Results

3.1. Optical Properties

Figure 1 shows the phosphorescence spectrum [7] of DNP in n-dodecane at 1.3 K. The high resolution which was not limited by the apparatus, enabled us to do an analysis of sites and vibrational bands. The vibrational analysis is shown in Table 1 while the site analysis is contained in Tables 1 and 2.

The occurrence of sites when molecules are embedded in Shpolskii matrices is a well known phenomenon [8—9]. Each of these sites possesses

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\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Int. & \( \nu \) [cm\(^{-1}\)] & \( \Delta \nu \) [cm\(^{-1}\)] & Possible assignment & Symmetry & \( k_y \) & \( k_z \) \\
\hline
vvs & 17538 & 17 & Site A, 0-0 & 1.00 & 1.00 & 0.06 & 0.02 \\
v & 17525 & 13 & Site B, 0-0 & 1.00 & 0.08 & 0.04 \\
w & 17451 & 87 & Site C, 0-0 & 1.00 & 0.11 & 0.05 \\
vw & 17396 & 142 & Site D, 0-0 & 1.00 & 0.09 & 0.04 \\
vw & 17358 & 180 & Site E, 0-0 & 1.00 & 0.12 & 0.06 \\
vw & 17313 & 225 & Site F, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 17250 & 288 & Site G, 0-0 & 1.00 & 0.09 & 0.04 \\
vw & 17217 & 341 & Site H, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 17127 & 411 & Site I, 0-0 & 1.00 & 0.21 & 0.09 \\
vw & 17088 & 450 & Site J, 0-0 & 1.00 & 0.09 & 0.04 \\
vw & 17008 & 530 & Site K, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16847 & 591 & Site L, 0-0 & 1.00 & 0.08 & 0.03 \\
vw & 16793 & 745 & Site M, 0-0 & 1.00 & 0.07 & 0.03 \\
vw & 16716 & 822 & Site N, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16659 & 879 & Site O, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16562 & 976 & Site P, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16383 & 1155 & Site Q, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16311 & 1227 & Site R, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16274 & 1264 & Site S, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16210 & 1328 & Site T, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 16135 & 1403 & Site U, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 15992 & 1546 & Site V, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 15967 & 1571 & Site W, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 15857 & 1581 & Site X, 0-0 & 1.00 & 0.10 & 0.03 \\
vw & 15826 & 1612 & Site Y, 0-0 & 1.00 & 0.10 & 0.03 \\
w & 15801 & 1637 & Site Z, 0-0 & 1.00 & 0.10 & 0.03 \\
\hline
\end{tabular}
\caption{Analysis of the phosphorescence spectrum of dinaphtho-(2'.3':1.2); (2''.3'':6.7)-pyrene in n-dodecane at 1.35 K.}
\end{table}
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its own phosphorescence spectrum. The experimentally recorded spectrum then is a superposition of a corresponding number of identical phosphorescence spectra which are shifted in energy relative to each other. Since each band shows the same multiplet structure, analysis of the spectrum is simple and straightforward, even if there are many lines.

In the case of DNP in n-dodecane no multiplet structure is observed. A straightforward interpretation therefore would identify the bands marked C, D and E as vibrational bands of the main site A. This would seem even more plausible since lower lying bands might be explained as combinations of these fundamentals. Such an interpretation, however, would be wrong. ODMR measurements prove the bands B, C, D and E to be 0—0-bands of further sites.

The ZFS of $T_1$ and the position of the 0—0 band depend on the interaction between molecules and matrix in the various sites. Figure 2 shows the ODMR-transitions between the two outer ZFL's in the bands indicated. From the difference in resonance frequencies it follows that the bands marked B, C, D and E are the 0—0-bands of 4 sites. The first vibronic band of site A is the one at 17313 cm$^{-1}$.

In a case like that of DNP/n-dodecane where the 0—0-band (17538 cm$^{-1}$) is much more intense than all other vibronic bands, sites with less radiative intensity can only be observed in their 0—0-bands. The expected multiplet structure will not be observed because of lacking intensity and optical measurements alone may lead to an incorrect interpretation of the spectrum.

Sometimes it is possible in such a case to recognize a site through its metastability [8]. This can be observed if the relative intensities of the bands are different for fast and slow cooling of the sample. For DNP/n-dodecane, however, sites A, B, C and D proved to be thermally stable and cannot be identified as sites by varying the cooling rate.

Table 1 shows the resulting vibrational analysis of the phosphorescence spectrum of DNP. The possible assignments listed in Table 1 together with the symmetry of the vibronic bands will be discussed in Section 3.2. The symmetry of the vibronic bands can be determined from a comparison [10] of the relative radiative rate constants $k_{xT}$, $k_{yT}$ and $k_{zT}$ and the group-theoretical analysis of the phosphorescence mechanisms. This analysis is summarized schematically in Table 4. The relative radiative rate constants were measured by means of MIDP-experiments [11] in the phosphorescence bands with sufficient intensity. 4—6 individual measurements with a high number of scans were taken in each band so the error margin does not exceed ±10%. These accurate radiative rate constants were necessary especially for the distinction between $b_{1g}$ and $b_{2g}$ vibrations as will be discussed in Section 4.2.

### 3.2. Zero Field Splitting and Kinetic Rate Constants

Table 2 shows the ZFS of $T_1$ in the five sites. Until now no quantitative relationship could be
deduced between the energetic position of $T_1$ and its ZFS. The behaviour of the $D$-parameter, however, may be understood in a qualitative way. $|D|$ is a measure of the spatial separation within the molecular plane of the triplet electrons. Because of the dipolar interaction of the two electrons $|D|$ increases with decreasing average distance between them and vice versa.

From the experimental results in Table 2 it can be seen that $|D|$ increases for larger triplet energy differences $T_1 - S_0$.

It is known [12] that for aromatic hydrocarbons in n-alcanes the absorption spectra are redshifted as compared to those in the gas phase. Since solute as well as solvent are non-polar the interactions causing this spectral shift are mainly London dispersive forces.

Thus the spectral shift of $T_1 - S_0$ from site A through site E as indicated in Table 2 seems to reflect an increase in interaction strength from site A through site E. With this an energetically more favourable average separation of the two electrons seems possible as shown by the decrease of $|D|$, due to the increasing influence of the solvent on the molecule's electronic structure.

Table 3 presents the kinetic data of population and depopulation of the ZFL's of $T_1$. They were determined by means of MIDP-experiments at 1.3 K where SLR could be neglected. The latter was confirmed by measuring the temperature dependence of the slowest decay rate $k_x$. Below 1.6 K $k_x$ remained constant within experimental error while above that temperature a slow increase could be seen. So the kinetic rate constants in Table 3 are the „true“ kinetic rate constants of DNP/n-dodecane.

The notation used is as follows: $k_i$ is the total decay rate of ZFL $t_i$ of $T_1$ to the ground state $S_0$; $K_i$ is the ISC rate for the population of $t_i$ from $S_1$, and $N_t$ denotes the stationary equilibrium population ratios.

The decay rate constants were determined for the sites A, B, C and E, whereas the weak intensity of site D precluded reliable measurements. For the same reason the ISC rates $K_i$ and the relative population numbers $N_i$ could not be determined in sites B, C, D and E (see Table 3).

4. Discussion

4.1. Signs of $|D|$ and $|E|$ and Symmetry of $T_1$.

The axis system was chosen according to Mulliken for $D_{2h}$ molecules as indicated in Figure 1. In this system the Hamiltonian for the ZFS can be written in the form:

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

For aromatic molecules it is known [13—15] that the out-of-plane level $l_x$ is the lowest in energy and therefore $D > 0$.

A Hückel calculation [16] gave $3B_{1u}$ orbital symmetry for $T_1$ of DNP. From the group theoretical matrix elements listed in Table 4 then it follows that radiative intensity of the 0—0-band comes only from $t_y$. The MIDP experiments in the 0—0-band showed that by inducing the $|D| + |E|$ transition and so repopulating the top ZFL the highest radiative rate constant was obtained; by inducing the $|D| - |E|$ transition and so measuring the radiative rate constant of the inner ZFL a markedly lower radiative rate constant was obtained. That means that the energetic order of the two in-plane levels must be $t_y > t_x$. In the axis system chosen the signs of $D$ and $E$ follow from the Hamiltonian as $D > 0$ and $E < 0$.

4.2. Radiative Decay of $T_1$ and Vibrational Bands

If the orbital symmetry of $T_1$ is known the radiative decay mechanisms of the 3 ZFL's into the vibrational bands of the ground state $S_0$ can be determined with the help of group-theoretical analysis [15, 17]. With the four mechanisms [18]

Table 3. Kinetic rate constants for the three ZFL's of $T_1$ of dinaphtho-(2’.3’.1.2): (2”’.3”’.6.7)-pyrene/n-dodecane.

<table>
<thead>
<tr>
<th>Site</th>
<th>$k_y$ [s$^{-1}$]</th>
<th>$k_z$ [s$^{-1}$]</th>
<th>$k_x$ [s$^{-1}$]</th>
<th>$K_y$</th>
<th>$K_z$</th>
<th>$K_x$</th>
<th>$N_y$</th>
<th>$N_z$</th>
<th>$N_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.97 ± 0.06</td>
<td>1.26 ± 0.15</td>
<td>0.15 ± 0.01</td>
<td>0.22</td>
<td>1.00</td>
<td>0.03</td>
<td>0.14</td>
<td>1.00</td>
<td>0.24</td>
</tr>
<tr>
<td>B</td>
<td>2.04 ± 0.08</td>
<td>1.41 ± 0.2</td>
<td>0.23 ± 0.021</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.30 ± 0.09</td>
<td>1.67 ± 0.22</td>
<td>0.23 ± 0.015</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2.22 ± 0.12</td>
<td>1.53 ± 0.2</td>
<td>0.23 ± 0.02</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Group theoretical matrix elements of the different SOC mechanisms for the lowest excited triplet state of a $D_{2h}$ molecule with $3B_{1u}$ orbital symmetry.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Matrix Element</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3$B_{1u}$($\pi \pi^*$)</td>
<td>$\langle T_{1u}</td>
<td>H_{SO}</td>
</tr>
<tr>
<td>$t_g(b_{2g})$</td>
<td>$3B_{1u} \rightarrow 1B_{3u}(\sigma \pi^*)$</td>
<td>one-centre contribution</td>
</tr>
<tr>
<td>$t_e(b_{1g})$</td>
<td>$3B_{1u} \rightarrow 1A_u(\sigma \pi^*)$</td>
<td>three-centre contribution</td>
</tr>
<tr>
<td>$t_g(b_{3g})$</td>
<td>$3B_{1u} \rightarrow 1A_g(\pi \pi^*)$</td>
<td>three-centre contribution</td>
</tr>
</tbody>
</table>

(1) direct spin-orbit coupling (SOC), SOC with vibronic coupling in the (2) singlet and (3) triplet manifold and (4) spin-vibronic coupling the decay scheme as pictured in Table 4 is obtained for a $3B_{1u}$ state of the $D_{2h}$ point group. In this decay scheme only those SOC mechanisms have been taken into account which connect $\pi \pi^*$ states with $\pi \sigma^*$ or $\sigma \pi^*$ states and in this way lead to important one-centre integrals ($\pi \sigma^*$ and $\sigma \pi^*$ states both will be denoted as $\sigma \pi^*$ in the following). So the only vibrational bands to be observed in the phosphorescence spectrum aside from the 0–0-band must have the symmetry $a_g$, $b_{1g}$, $b_{2g}$ or $b_{3g}$. By comparison of the radiative intensities according to Table 4 with those obtained experimentally the symmetries and radiative mechanisms of the vibrational bands can be determined.

However, the distinction between the two out-of-plane vibrations $b_{1g}$ and $b_{2g}$ proves to be rather difficult considering the radiative rate constants alone. $b_{1g}$ and $b_{2g}$ both obtain their radiative intensity mainly from $t_g$ and $t_e$. On the other hand $b_{1g}$ vibrational bands should be the only ones to get intensity from $t_e$ too. This is due to spin-vibronic coupling of $t_e$ with a $1B_{3u}(\sigma \pi^*)$ state through a $b_{1g}$ vibration and SOC with vibronic ($b_{1g}$) coupling in the triplet manifold

$$\{3B_{1u} \rightarrow \frac{\partial H_{SO}}{\partial Q} | S_m \rangle \langle S_m | \hat{D} | S_0 \rangle \rightarrow 1B_{3u}(\sigma \pi^*) \rightarrow 1A_g \}$$

both mechanisms leading to one-centre integrals of the SOC. According to Albrecht [18], however, spin-vibronic coupling is smaller than the mechanisms (1)–(3) and the magnitude of SOC matrix elements between two $\sigma \pi^*$ states as compared to those between $\pi \pi^*$ and $\sigma \pi^*$ states [19] is unknown. Still, because of their one-centre contributions the SOC matrix elements between two $\sigma \pi^*$ states should be greater than those between two $\pi \pi^*$ states. Consequently one should be able to identify $b_{1g}$ vibrational bands as the only ones that get little but detectable intensity from $t_e$.

To date this possibility to distinguish between the $b_{1g}$ and $b_{2g}$ vibrations has not been utilized [10, 15, 17]. In the case of DNP reported here it is of considerable importance. Due to extremely weak phosphorescence intensity in the single vibrational bands and depolarization effects in our optical system photoselection experiments failed. Such experiments could have helped in the distinction of the two vibrational symmetries through the
different polarizations of radiation from $t_4$ and $t_2$ in $b_{1g}$ and $b_{2g}$ vibrational bands. Without the photoselection technique applicable there remains only the $k_{x^2}$-rate to distinguish between the $b_{1g}$ and $b_{2g}$ symmetries.

Table 1 summarizes the experimentally determined relative radiative rate constants $k_{y^2}$, $k_{x^2}$ and $k_{z^2}$. From the experimental data it follows that the vibrational band at 16383 cm$^{-1}$ is the only one with a pronounced $k_{x^2}$-rate obtaining additional intensity from $t_4$ and $t_2$. So according to the foregoing discussion this band is of $b_{1g}$ symmetry and the qualitative theoretical considerations seem to be confirmed rather well.

The symmetries of the other vibrational bands follow from Table 4 and the values of $k_{y^2}$, $k_{x^2}$ and $k_{z^2}$.

It is well known [20—24] that independent of their degree of annelation for pure aromatic hydrocarbons there exist quite pronounced frequency regions for various types of vibrations. If this information is combined with the results of the symmetry analysis based on the ODMR measurements it is possible to arrive at some conclusions concerning the type of vibration giving rise to each single phosphorescence band.

The normal modes $v_1$—$v_6$ which are of $a_1$ or $b_{3g}$ symmetry and accordingly correspond to vibrations within the molecular plane, all belong to the region of C—C bending (parallel: ||) vibrations [20] and lead to skeletal distortions.

The normal modes $v_7$—$v_9$ can be attributed to C—H-wagging vibrations. This follows from their $b_{2g}$ symmetry corresponding to out-of-plane vibrations and their frequency. Extensive investigations [23—27] have shown that C—H-wagging vibrations in which adjacent H-atoms oscillate in phase occur independent of the degree of annelation between 700 cm$^{-1}$ and 900 cm$^{-1}$.

The normal mode $v_7 = 745$ cm$^{-1}$ can be explained as a so called „quartet“-band [23] which has four H-atoms oscillating in phase and which can be found in the region 735 cm$^{-1}$—770 cm$^{-1}$ in IR-spectra. In the case of DNP $v_7$ corresponds to an in-phase oscillation of the 4 adjacent H-atoms at the outer benzene rings of the two annelated naphthalene skeletons.

The normal mode $v_8 = 822$ cm$^{-1}$ then might correspond to a so called „trio“-CH-wagging vibration [23]. This type of vibration is observed between 750 cm$^{-1}$ and 810 cm$^{-1}$ in the IR-spectra.

The „solo“-CH-wagging vibrations [23] occurring between 860 cm$^{-1}$—900 cm$^{-1}$ could explain the normal mode $v_9 = 879$ cm$^{-1}$ in the DNP-molecule. This band is relatively intense corresponding to the four independent „solo“-oscillators in DNP.

The vibrations $v_{10} = 976$ cm$^{-1}$, $v_{11} = 1155$ cm$^{-1}$ and $v_{12} = 1227$ cm$^{-1}$ have been attributed to normal modes although they could be explained as combinations. This has not been done since these combinations do not seem to be realistic because of symmetry and intensity reasons. According to their symmetry the normal modes $v_{10}$ and $v_{11}$ probably are C—H-bending (perpendicular: \(\perp\)) vibrations whereas $v_{12}$ is a C—H-bending(\(\parallel\)) vibration typical of this frequency region [20].

Another typical vibration in aromatic molecules is the so called gamma-C—C stretching vibration [6, 7, 22] which has $a_1$-symmetry and is located between 1350 cm$^{-1}$ and 1400 cm$^{-1}$. The vibration $v_{13} = 1403$ cm$^{-1}$ in DNP might be attributed to such a gamma vibration. However, a combination is also possible. A clear distinction is not feasible on the basis of the presently available experimental data.

The normal modes $v_{15}$ and $v_{16}$ unambiguously can be identified as C—C stretching vibrations [20] whereas the frequency of $v_{14}$ seems too high for a $b_{3g}$-vibration and no particular type of vibration is ascribed to this band.

4.3. Radiationless Processes

It has been maintained in numerous communications [5, 6] that in the case of molecules showing very weak phosphorescence intensity the total decay rates $k_t$ in good approximation can be taken as the nonradiative decay rates $k_{t^*}$. The same arguments also apply in the case of DNP.

So the radiationless decay and the population of the three ZFL's can be described by means of the total decay rates $k_t$ and the ISC-rates $K_i$, and a behaviour typical of aromatic molecules becomes apparent [5, 6, 19, 25]: The two in-plane ZFL's are characterized by distinctly faster radiationless processes than the out-of-plane level. For the sites A, B, C and E a ratio of $15 \leq (k_y + k_d)/k_x \leq 20$ is obtained in good agreement with theoretical calculations [19] which give values of 10—30 for pure aromatic hydrocarbons. The differences in radiationless decay rates between in-plane and out-of-plane ZFL's are explained by the fact that for the in-plane levels one-centre integrals are
obtained already in first order of SOC whereas only in second order for the out-of-plane level.

In an earlier study on coronene derivatives [6] we found that the ratio of the decay rates of in-plane and out-of-plane levels varied for the different sites and we were able to find a correlation with the molecule’s planarity in the different sites.

A similar behaviour is observed here for DNP where the \((k_y + k_z)/k_x\) ratio is greatest for site A, and all other sites clearly show lower values. However, for sites B, C and E the \(k_x\)-decay rates cannot be determined with great precision because these sites are only observed in their 0-0-band where radiative intensity originates almost exclusively in \(t_y\). Therefore an MIDP-signal of the \(t_x - t_z\)-transition is hard to detect. The decay of such a signal would give a much more precise value for \(k_y\) than the MIDP-analysis of \(t_y - t_z\) transition signals since the decay rates of \(t_z\) and \(t_y\) are almost equal. So because of the relatively large error in the measurement of \(k_z\) conclusions following from the value of \((k_y + k_z)/k_x\) with respect to planarity of the molecules in the different sites have to be taken with some caution. Still it seems rather obvious that the difference between in-plane and out-of-plane decay rates (the difference being due to the molecular plane as a symmetry element) is clearly more pronounced in site A than in site B, C and D. Therefore planarity of the molecule seems to be better conserved in site A than in sites B, C and D.

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