Intramolecular Electron Transfer in Nonconjugated Polyenes

Michael C. Böhm
Institut für Organische Chemie der Universität Heidelberg

Z. Naturforsch. 36a, 859—867 (1981); received June 15, 1981

The probability of hole-propagation of initially prepared vacancies in 1,5-hexadiene (1) and 1,6-heptadiene (2) as well as the transfer mechanisms in 1 and 2 are studied by means of time-dependent perturbation theory. Times of equilibration of about $10^{-12}$ sec are calculated. Local perturbations in the $\pi$ moieties are efficiently transmitted via CH-$\sigma$ states while CC-$\sigma$ functions and the direct transfer channel are less important. The theoretical key step consist in an unitary transformation of the canonical molecular orbitals (CMO’s) with the diagonal Fock operator into a set of one-electron states forming a transport-type Fockian, $F_{\text{TET}}$, where only a few matrix elements (between the evolving orbitals and a set of messenger states) differ from zero.

1. Introduction

Experimental investigations of intramolecular electron transfer processes have found enlarged interest in the recent years. Typical examples where these transport phenomena have been studied are organic polymers [1], bridged aromatic radicals [2], polynuclear transition metal derivatives [3], biological species with transition metal centers as active sites [4] as well as the various organic and organometallic systems able to the photoelectrochemical conversion of light energy [5]. The existing theoretical approaches for the intramolecular electron transport processes roughly can be devided into three classes (I, II and III). Class I is based on the quasiclassical electron motion between two potential wells that are devided by an energy barrier; this theory commonly is called tunnel electron transfer (TET) model [6]. Two-site tunneling descriptions of class II are predominantly vibrational models where the electronic contribution is added to the basis equations only as constant factor; these models give no insight into the time-evolution of instationary electronic states [7]. Theoretical methods belonging to class III once again are purely electronical approaches that are based on an approximative Hamiltonian of the Hubbard-type with on-site Coulomb terms and inter-site one-electron interaction integrals [8].

The presented theoretical methods (I, II, III) however have a common drawback in spite of their individual success. The parameters of the different theoretical approaches to intramolecular electron transfer are only estimated phenomenologically but they are not related to well defined quantum-chemical procedures (e.g. variational procedure, SCF Hartree-Fock (HF) approximation, descriptions beyond the independent electron picture). The connecting link between the convenient molecular orbital (MO) representation, the canonical MO’s, and a suitable Hamiltonian or Fock-type operator for electron transfer processes is missing in the convenient transport theories.

In a recent paper we have shown that the canonical molecular orbitals with the associated one-electron energies, $\epsilon_i$, unambiguously can be transformed into a set of one-electron states, selfenergies and interaction terms between instationary localized and stationary delocalized orbitals that represent a proper choice for a Fock operator forming a basis for the investigation of the time-evolution of molecular hole-states or vacancies [9]. The structure of the transformed Fockian corresponds to the Hubbard Hamiltonian [10], diagonal and off-diagonal elements are determined via unitary transformations starting from the diagonal CMO representation; the conceptional shortcomings of the approximative Hubbard operator therefore are avoided.

In the present publication we want to investigate the transfer times and transport mechanisms in simple nonconjugated dienes by means of our recently developed transfer Fockian. In detail we have studied the time-evolution of $\pi$-orbitals forming an electron-hole pair in 1,5-hexadiene (1) in different molecular conformations; the two extreme geometries (1a: trans-trans and 1b: cis-...
trans) are displayed below. The theoretical findings observed for the hexadiene compound are compared with results obtained for the all-trans conformation of 1,6-heptadiene (2).

Computational framework of this investigation is a recently designed INDO MO model [11]. Standard bondlengths and bondangles have been used for 1 and 2 [12].

2. Theory

It is assumed that a set of canonical molecular orbitals \( \Phi_i \) of a closed shell system with paired spins has been obtained by the convenient Hartree-Fock procedure. The Fock operator in the \( \Phi_i \) basis, \( F_{\text{CMO}} \), is defined in Eq. (1) where \( a_i^+ \) and \( a_i^\dagger \) symbolize the creation and destruction operator of the \( i \)'th one-electron state in the CMO basis.

\[
F_{\text{CMO}} = \sum_i \varepsilon_i a_i^+ a_i^\dagger, \quad i = 1, 2, \ldots, N. \quad (1)
\]

In a subsequent step the delocalized stationary CMO's are transformed into a set of localized molecular orbitals (Equation (2)). \( \phi \) and \( q \) are the column vector of the CMO's \( \Phi_i \) (3) and the LMO's \( q_i \) (4).

\[
\phi = (\Phi_1 \Phi_2 \ldots \Phi_N)^T, \quad (3)
\]

\[
q = (q_1 q_2 \ldots q_N)^T. \quad (4)
\]

In the present study we have used the intrinsic Edmiston-Ruedenberg localization procedure [13] for the orthogonal transformation (2). Other localization strategies are discussed in [9].

Due to (2) the diagonal Fock operator, \( F_{\text{CMO}} \), is transformed into a Fockian forming a full matrix.

\[
F_{\text{LMO}} = L F_{\text{CMO}} L^T, \quad (5)
\]

\[
F_{\text{LMO}} = \sum_i \varepsilon_i a_i^+ a_i^\dagger + \sum_{i \neq j} \varepsilon_{ij} a_i^+ a_j^\dagger. \quad (6)
\]

The diagonal and off-diagonal elements in (6) are associated to the localized one-electron states \( q_i \). To derive a Fock operator of a generalized Hubbard-type the cross-terms \( \varepsilon_{ik} \) and \( \varepsilon_{jk} \) between the preselected instationary electron-hole pair \( q_i \) and \( q_j \) and the remaining set of localized orbitals \( q_k (k \neq i, j) \) are set equal to zero forming the decoupled operator \( F_{ij}^{\text{DEC}} \).

\[
F_{ij}^{\text{DEC}} = \sum_i \varepsilon_i a_i^+ a_i^\dagger + \sum_{k \neq i} \varepsilon_{ik} a_k^+ a_k. \quad (7)
\]

\( F_{ij}^{\text{DEC}} \) is a full matrix with vanishing off-diagonal elements in the \( i \)'th and \( j \)'th row and column. Diagonalization of \( F_{ij}^{\text{DEC}} \) results in the eigenvectors \( D_{ij} \) of the decoupled Fockian. The back transformation (8) of \( F_{\text{LMO}} \) leads to the desired transport Fock operator \( F_{HT} \) with nonvanishing elements in the \( i \)'th and \( j \)'th row and column.

\[
F_{HT} = D_{ij} F_{\text{LMO}} D_{ij}^T, \quad (8)
\]

\[
F_{HT} = \sum_i \varepsilon_i a_i^+ a_i^\dagger + \sum_k \varepsilon_k a_k^+ a_k
+ \sum_{k \neq i} \varepsilon_{ik} a_k^+ a_i + \varepsilon_{ij} a_i^+ a_j. \quad (9)
\]

The various increments \( \varepsilon_i \), \( \varepsilon_k \) and \( \varepsilon_{kj} \) in (9) can be rationalized in physically relevant pictures. \( \varepsilon_i \) and \( \varepsilon_k \) are the one-electron energies of the localized states \( q_i \) and \( q_j \) in their own potential field and the field of the atomic cores belonging to the \( i \)'th and \( j \)'th localized domain. \( \varepsilon_k (k \neq i, j) \) stands for the \((N - 2)\) one-electron energies of a diagonal MO subspace (dimension \((N - 2)\)). The lifetimes in the \( k \)-domain is infinite. According to the convenient HF averaging procedure each electron in the \( k \)-set is moving in the field of \((N - 3)\) electrons; the \( k \)-th self-energy and the influence of \( q_i \) and \( q_j \) are removed from the potential experienced within this one-electron set. The MO basis of the \((N - 2)\) \( k \)-states is symbolized by \( \lambda_k (k = 1, 2 \ldots (N - 2)) \).
The cross-elements \( \varepsilon_{ik}/\varepsilon_{kj} \) are the interaction terms between the two localized HF states \( q_i \) and \( q_j \) with the remaining \( \lambda_k \) functions. The MO basis of \( F^{HT} \) therefore is of a mixed type as two localized one-electron functions and \((N-2)\) delocalized orbitals are combined to basis (10) of the Hubbard-like Fock operator \( F^{HT} \).

\[
\lambda^{HT} = \begin{pmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\lambda_{(N-2)} \\
q_i \\
q_j
\end{pmatrix} = (\lambda_1 \lambda_2 \ldots \lambda_{(N-2)} q_i q_j)^T.
\] (10)

Various other choices for the \( \lambda^{HT}(t) \) states and the mounted Hilbert spaces together with the necessary decoupling steps are presented in our previous paper [9].

The time-dependent states \( q_i(t) \) and \( q_j(t) \) of \( \lambda^{HT}(t) \) are developed by means of the Dirac variation of constants [14].

\[
q_i(t) = \sum_k c_k(t) \lambda_k.
\] (17)

To study the time-evolution between the electron-hole pair \( q_i, q_j \) we define the time-dependent one-electron states \( \lambda^{HT}(t) \) by means of (16):

\[
U_{ND} = \sum_{n=0}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int dt' \int dt'' \ldots \int dt'^{(n-1)} F^{HT}_{ND,1}(t') F^{HT}_{ND,1}(t'') \ldots F^{HT}_{ND,1}(t'^{(n-1)}),
\] (18)

\[
S_{ij} = S_{ij}^{(1)} + S_{ij}^{(2)},
\] (20)

\[
S_{ij}^{(1)} = \left| \left( i\hbar \right)^{-1} \int dt' \exp(i\omega_{k} t') \varepsilon_{ij} \right|^2,
\] (21)

\[
S_{ij}^{(2)} = \sum_{k=1}^{N} \left| \left( i\hbar \right)^{-2} \int dt' \int dt'' \exp(i\omega_{j} t' + i\omega_{k} t'') \varepsilon_{ik} \varepsilon_{kj} \right|^2,
\] (22)

\[
\omega_{ij} = (\varepsilon_i - \varepsilon_j) \hbar.
\] (23)
\( S^{(1)}_{ij} \) is the direct transfer channel of the evolving electron-hole pair \( q_i \) and \( q_j \). It is proportional to the cross-element, \( \epsilon_{ij} \), between the two localized domains and depends on the Bohr frequency \( \omega_{ij} \) between the initially \((t=0)\) prepared hole-state (vacancy) and the electron state \( q_j \). In second order \( q_i \) and \( q_j \) are coupled by means of the messenger states \( \lambda_k \) forming \((N-2)\) indirect transfer channels in contrast to a single direct transfer path. The explicit formulas for the direct, \( S^{(1)}_{ij} \), and indirect, \( S^{(2)}_{ij} \), contributions to the net probability of hole-propagation under non resonant and resonant (vanishing Bohr frequencies) transfer conditions are given in [9].

Due to the Dirac variation (17) only the constants \( c_k(t) \) change in time. In the present work we have studied the hole-propagation from the stationary hole distribution (24) to the hole-distribution (25) where the vacancy \( q_i \) has been filled by the donor-state \( q_j \). Obviously \( c_i(t=0) = 0 \) while the donor-function \( q_j \) fulfills \( c_j(t=0) = 1 \).

\[
| \lambda_1 \lambda_2 \ldots \lambda_i^{\text{hole}} \lambda_j^{\text{donor}} |, \quad c_i(t) = 0, \quad c_j(t) = 1, \quad t = \sigma, \tag{24}
\]

\[
| \lambda_1 \lambda_2 \ldots \lambda_i^{\text{donor}} \lambda_j^{\text{hole}} |, \quad c_i(t') = 1, \quad c_j(t') = \sigma, \tag{25}
\]

\[
c_i(T_{c,50}) = c_j(T_{c,50}) = 1/\sqrt{2}. \tag{26}
\]

In (26) the time of hole-equilibration among the \( q_i/q_j \) MO set is defined.

If reorganizational rearrangements in the \( i' \)th localized hole-domain are not taken into account, the orbital energies of the transformed closed shell Fockian are directly used in the calculation of \( S_{ij} \). In the field of photoelectron spectroscopy this approximation is known as Koopmans' theorem [17]. On the other hand we have developed a simple method taking into account the combined effects of electron relaxation and correlation in the vicinity of the prepared vacancy [9]; theoretical background of this additional hole-potential is a generalization of Slater’s concept of nonintegral occupation numbers [18] successfully applied in the transition state theory within the \( X_2 \) approximation [19] and the transition operator method [20] as LCAO counterpart to the statistical approach.

Reorganization energies for the \( i' \)th prepared hole-state and the time-evoluting electron-state \( q_j \) are dynamically coupled by means of the relations (27) and (28) which obey the rules of conservation of energy:

\[
\epsilon_i(t_n) = \epsilon_i(t_{n-1}) + (1 - S_{ij}(t_{n-1})) \cdot \Delta t, \tag{27}
\]

\[
\epsilon_j(t_n) = \epsilon_j(t_{n-1}) + S_{ij}(t_{n-1}) \cdot \Delta t. \tag{28}
\]

\( \epsilon_i(t_n) \) and \( \epsilon_j(t_n) \) are the one-electron energies of the \( i' \)th hole- and \( j' \)th particle-state in the \( n' \)th integration step, \((1 - S_{ij}(t_{n-1}))\) is the probability for finding the initially prepared \((t=0)\) hole-state in the \( i' \)th domain at the time \( t_{n-1} \) while \( S_{ij}(t_{n-1}) \) is the probability that the \( i' \)th hole-state has been propagated to the \( j' \)th electron-function, \( \Delta t \) is the reorganizational correction in the limit of full hole-localization. The determination of \( \Delta t \) for decoupled bonds, lone-pairs or metal d orbitals is described in [9]. The dynamic coupling between \( q_i \) and \( q_j \) is clearly recognized in (27) and (28). At \( t=0 \) \( S_{ij}(t=0) = 0 \) and reorganizational rearrangements are only observed in the \( i' \)th hole-domain. With increasing time (increasing probability for the hole-propagation) the net deviations from \( \epsilon_i \) in the hole-state \( q_i \) are asymptotically reduced while enlarged reorganization effects are encountered in the \( j' \)th donor-state.

The just developed theory is only valid if the intramolecular electron transfer events are faster than about \( 10^{-14} \) sec (the shortest vibrational periods in organic and organometallic molecules) as in slower transfer processes the motion of the electrons is not independent of the nuclear motion (Born-Oppenheimer approximation). In the limit of transfer times \( > 10^{-14} \) sec the vibrational sub-Hamiltonian and the electron-phonon interaction of the Fröhlich-type [21] must be taken into account in the time-evolution of the electron-hole pair. Furthermore the coupling (tunneling) elements \( \epsilon_{ik} \) and \( \epsilon_{jk} \) must be small enough to be treated by means of the perturbational expansion (18).

3. Calculations

In the case of the 1,5-hexadiene 1 we have studied the time-evolution between the electron-hole pair formed by the two localized \( \pi \) orbitals in five conformations. In the case of the two extreme trans-trans (1a) and cis-trans (1b) conformation only two CH-\( \sigma \) orbitals (see Fig. 1) can act as messenger states for the transfer of the \( \pi \) vacancy. In the conformations with a torsional angle \( \alpha = 135^\circ, 90^\circ \) and \( 45^\circ \) between both \( \pi \) moieties the hole-transfer additionally can be submitted also via
Table 1. Localized molecular orbitals of 1,5-hexadiene in the 90° conformation.

<table>
<thead>
<tr>
<th>MO-Type</th>
<th>Number</th>
<th>$\epsilon_{LMO}$ (eV)</th>
<th>Impurities %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-σ</td>
<td>C1C2=C3C4</td>
<td>2</td>
<td>-22.53</td>
</tr>
<tr>
<td></td>
<td>C3C4=C4C5</td>
<td>2</td>
<td>-21.83</td>
</tr>
<tr>
<td></td>
<td>C1C4</td>
<td>1</td>
<td>-20.43</td>
</tr>
<tr>
<td>CH-σ</td>
<td>C4H3=C5H8</td>
<td>2</td>
<td>-20.83</td>
</tr>
<tr>
<td></td>
<td>C4H1=C5H9</td>
<td>2</td>
<td>-20.60</td>
</tr>
<tr>
<td></td>
<td>C1H2=C5H10</td>
<td>2</td>
<td>-20.47</td>
</tr>
<tr>
<td></td>
<td>C2H4=C3H5 = C4H6=C4H7</td>
<td>4</td>
<td>-20.25</td>
</tr>
<tr>
<td>CH-π</td>
<td>C1C2=C3C4</td>
<td>2</td>
<td>-11.57</td>
</tr>
</tbody>
</table>

molecular transfer. The transformed one-electron states representing the basis of the $F^{HT}$ operator are summarized in Table 2. The diagonal elements ($F_{ik}^{HT}$) as well as the tunneling increments ($\epsilon_{ik}$, $\epsilon_{jk}$, $\epsilon_{ij}$) of the perturbational operator $F^{ND}$ are given in column 4, 5 and 6. The MO's of the $\lambda_k$ set (MO 1—MO 15) transform according to the irreducible representations of the $C_2$ point group. MO 16 and MO 17 are the two instationary localized $\pi$-functions forming the time-evoluting electron-hole pair. MO 1, 2, 3, 9 and 15 are predominantly of CC-σ character while the remaining delocalized $\lambda_k$ states correspond to the various CH-σ linear combinations.

In Tables 3 and 4 we have collected characteristic quantities for the transfer dynamics in 1,5-hexadiene for torsional angles of 180°, 135°, 0°, and 90°.
Table 3. Times of localization in 1,5-hexadine (1) of an initially prepared hole-state at \( q_i \). \( T_{c.25} \) and \( T_{c.50} \) represent the times necessary that 25% and 50% of the \( i \)th hole-state has been transferred to the \( j \)th electron state. The \( T_{c.n} \) values have been obtained in the framework of an independent electron model.

<table>
<thead>
<tr>
<th>( \alpha [\degree] )</th>
<th>( T_{c.25} ) (sec)</th>
<th>( T_{c.50} ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>( 6.31 \times 10^{-16} )</td>
<td>( 8.95 \times 10^{-16} )</td>
</tr>
<tr>
<td>135</td>
<td>( 7.72 \times 10^{-16} )</td>
<td>( 9.60 \times 10^{-16} )</td>
</tr>
<tr>
<td>90</td>
<td>( 1.00 \times 10^{-15} )</td>
<td>( 1.36 \times 10^{-15} )</td>
</tr>
<tr>
<td>45</td>
<td>( 8.83 \times 10^{-16} )</td>
<td>( 1.13 \times 10^{-15} )</td>
</tr>
<tr>
<td>0</td>
<td>( 5.27 \times 10^{-16} )</td>
<td>( 7.45 \times 10^{-16} )</td>
</tr>
</tbody>
</table>

Table 4. Times of localization in 1,5-hexadiene (1) calculated under the inclusion of reorganizational rearrangements via the \( \Delta_l \) potential; see legend Table 3.

<table>
<thead>
<tr>
<th>( \alpha [\degree] )</th>
<th>( T_{c.25} ) (sec)</th>
<th>( T_{c.50} ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>( 7.04 \times 10^{-16} )</td>
<td>( 8.66 \times 10^{-16} )</td>
</tr>
<tr>
<td>135</td>
<td>( 8.10 \times 10^{-16} )</td>
<td>( 1.01 \times 10^{-15} )</td>
</tr>
<tr>
<td>90</td>
<td>( 1.10 \times 10^{-15} )</td>
<td>( 1.64 \times 10^{-15} )</td>
</tr>
<tr>
<td>45</td>
<td>( 9.39 \times 10^{-15} )</td>
<td>( 1.26 \times 10^{-15} )</td>
</tr>
<tr>
<td>0</td>
<td>( 6.12 \times 10^{-16} )</td>
<td>( 7.22 \times 10^{-16} )</td>
</tr>
</tbody>
</table>

90°, 45° and 0° respectively. To evade the well known convergence problems in time-dependent perturbation theory due to near-resonant transfer channels and due to the irreversible ansatz \( q_i \) (hole-state) \( \rightarrow \) \( q_j \) (electron-state) [15, 22] we have displayed the times corresponding to a probability of hole-propagation of 25% (\( T_{c.25} \)) and 50% (\( T_{c.50} \)); the latter quantity is associated to the equilibration of the initially prepared \( q_i \) hole-state within the evolving \( q_i, q_j \) pair. The \( T_{c.n} \) parameters in Tab. 3 have been obtained within a Koopmans-related independent electron approach while the values in Tab. 4 answer the additional reorganizational potential \( \Delta_l \) within \( q_i \) and \( q_j \). It is seen that the \( \Delta_l \) corrections are only of minor importance in the transfer process; the \( T_{c.n} \) quantities are enlarged by about 10—15% if relaxation and correlation effects are taken into account. This result differs dramatically from binuclear transition metal compounds where pronounced reorganization effects in the \( i \)’th hole-domain prevent the intramolecular transfer process by means of purely electronic contributions, the hopping event is possible only by the coupling to molecular vibrations [9].

The results in Tab. 3 and 4 clearly display that the \( T_{c.n} \) values are strongly dependent from the molecular conformation. The fastest transfer events are possible in the case of the two planar conformations \( 1b \) (cis-trans) and \( 1a \) (trans-trans). The largest \( T_{c.n} \) values are predicted for the 90° conformation differing by a factor of 2 from the \( T_{c.n} \) parameters of \( 1a \) and \( 1b \). The calculated transfer times obviously are in an interval where the electronic motion (\( 10^{-15} \) sec) is independent from the nuclear vibrations. The INDO-based transfer times in the nonconjugated diene 1 exceed the times of localization in a conjugated \( \pi \)-system (e.g. benzene) by about a power of ten (\( 0.8—2.4 \times 10^{-16} \) sec) [23].

To rationalize the \( \alpha \)-dependent \( T_{c.n} \) values we have collected the contributions from the individual transfer channels (direct and indirect via the \( \lambda_k \) messenger states) in Tables 5 to 9 for the various 1,5-hexadiene conformations. The separation between the central C-atoms \( C_2 \) and \( C_5 \) of the two double bonds corresponds to 3.84, 3.68, 3.26, 2.78 and 2.55 Å for the different torsional angles \( \alpha \) (180°, 135°, 90°, 45° and 0°). In the case of \( \alpha = 90^\circ \), 45° and 0°, respectively. To evade the well known convergence problems in time-dependent perturbation theory due to near-resonant transfer channels and due to the irreversible ansatz \( q_i \) (hole-state) \( \rightarrow q_j \) (electron-state) [15, 22] we have displayed the times corresponding to a probability of hole-propagation of 25% (\( T_{c.25} \)) and 50% (\( T_{c.50} \)); the latter quantity is associated to the equilibration of the initially prepared \( q_i \) hole-state within the evolving \( q_i, q_j \) pair. The \( T_{c.n} \) parameters in Tab. 3 have been obtained within a Koopmans-related independent electron approach while the values in Tab. 4 answer the additional reorganizational potential \( \Delta_l \) within \( q_i \) and \( q_j \). It is seen that the \( \Delta_l \) corrections are only of minor importance in the transfer process; the \( T_{c.n} \) quantities are enlarged by about 10—15% if relaxation and correlation effects are taken into account. This result differs dramatically from binuclear transition metal compounds where pronounced reorganization effects in the \( i \)’th hole-domain prevent the intramolecular transfer process by means of purely electronic contributions, the hopping event is possible only by the coupling to molecular vibrations [9].

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and \( \alpha = 0^\circ \) only three available transfer channels (direct and two indirect ones) allow the hole-propagation. In the all-trans conformation 1a the direct channel ("through space" interaction [24]) contributes with 0.03% to the net transfer. In 1b the "through space" path is raised to 7.9% while the most important messenger state ("through bond" coupling [24]) is the antisymmetric CH-cr linear combination (MO 12).

For \( \alpha = 135^\circ, 90^\circ \) and 45° additional CH-cr and CC-cr channels are opened for the intramolecular hole-transport. In Table 6 it is seen that predominantly one messenger state (MO 12, CH-\( \sigma \)) is responsible for the transfer mechanism in the 135° conformation while several transmitter paths contribute with comparable weight in the 90° and 45° geometry. Table 7 indicates that the direct coupling between \( \varphi_i \) and \( \varphi_j \) is most efficient in the 90° 1,5-hexadiene where the direct channel contributes with 10.4% to the net transfer probability. The direct overlap between the two localized \( \pi \)-domains with perpendicular orientation here exceeds the "through space" coupling encountered in the various other geometries (see Figure 2).

![Fig. 2. Orientation of the electron-hole pair \( \varphi_i, \varphi_j \) in the 90° conformation of 1,5-hexadiene.](image)

In Table 10 we have summarized the contributions of the three transfer types (direct, indirect via CH-cr channels and indirect via CC-cr channels) of 1 in the different molecular conformations. It is seen that CC-cr messenger states only contribute to the transfer process in the 90° system while the CC-\( \sigma \) participation in the remaining orientations is lower than 1.5% (135° and 45°) and zero in the planar dienes 1a and 1b respectively. The enlarged \( T_c \) parameters for \( \alpha = 90^\circ \) thus are the result of a reduction of the available CH-cr channels and a magnification of the less efficient CC-cr transmitter paths. In Table 2 it is shown that the coupling terms between CC-\( \sigma \) and \( \varphi_i, \varphi_j \) are smaller than the tunnel elements of the localized states to the CH-\( \sigma \) messenger set.

In the all-trans conformation 2 of 1,6-heptadiene the central C atoms of the two \( \pi \) orbitals are separated by 3.86 Å. Three symmetry adapted CH-\( \sigma \) and CC-\( \sigma \) channels are opened for the intramolecular hole-transport. According to the theoretical approach \( T_{c,25} \) and \( T_{c,50} \) values of 7.18 \( \times 10^{-16} \) sec (6.72 \( \times 10^{-16} \) sec) and 1.02 \( \times 10^{-15} \) sec (1.13 \( \times 10^{-15} \) sec) are predicted for the independent electron model and the dynamically coupled extended (reorganization) approach indicating the better interference between the transfer amplitudes at \( T_{c,25} \) for the latter procedure. The calculated localization times of 2 are close to the \( T_{c,n} \) values of 1 which means that the probability of hole-propagation is independent of the length of the saturated C-center chain separating the \( \pi \)-moieties. The same conclusion has been observed in a theoretical treatment for intramolecular transfer processes that is called resonance interaction under donor-acceptor electron transfer (DAET) developed by Petrov and coworkers [25].

The contributions of the four transfer channels available in 2 are given in Tab. 11, a schematical
Table 11. Transfer channels in the all-trans conformation of 1,6-heptadiene.

<table>
<thead>
<tr>
<th>MO Nr. + Type</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 CH-σ</td>
<td>12.44%</td>
</tr>
<tr>
<td>12 CH-σ</td>
<td>73.57%</td>
</tr>
<tr>
<td>14 CH-σ</td>
<td>13.98%</td>
</tr>
<tr>
<td>direct</td>
<td>&lt;0.01%</td>
</tr>
</tbody>
</table>

representation of the CH-σ messenger states is displayed in Figure 3. It is seen that the direct (“through space”) transfer is of negligible importance, the predominant contribution is due to $\lambda_{12}$ where large cross-elements (see Fig. 3) and small Bohr frequencies both allow an efficient “through bond” coupling for the evolving electron-hole pair. As result of the smaller LCAO amplitudes at C3 and C5 within the two symmetrical CH-σ combinations, $\lambda_8$ and $\lambda_{14}$, the transfer channels via these states are less important.

4. Conclusions

It has been demonstrated that the delocalization of hole-states or vacancies in nonconjugated $\pi$-systems is effectively transmitted by means of CH-σ messenger states, the contribution due to the direct interaction between the localized electron- and hole-state does not contribute significantly to the net probability of hole-propagation. The transfer times are strongly influenced by the mutual orientation of the $\pi$-domains. A reduction of the coupling strength to the CH-σ states and available CC-σ channels results in less efficient transmitter capabilities. The predicted $T_{e,n}$ parameters of about $10^{-15}$ sec should be compared with localization times of $10^{-16}$ sec in conjugated $\pi$-systems and $10^{-14}$ sec obtained for 3d orbitals in bridged binuclear transition metal compounds [9]. The reduction of the cross-elements between the strongly localized 3d evolving states and the ligand one-electron set leads to slower transfer rates.

Acknowledgement

The work has been supported by the Stiftung Volkswagenwerk. The assistance of Mrs. H. Wellnitz in the preparation of the manuscript is gratefully acknowledged.