Intramolecular Electron Transfer in Nonconjugated Polyenes

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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 equibrilation of about 10^{-15} sec are calculated. Local perturbations in the π moieties are efficiently transmitted via CH-σ states while CC-σ 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^{HT}, where only a few matrix elements (between the evoluting 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, ε_i', unambiguously can be transformed into a set of one-electron states, self-energies 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 π-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-

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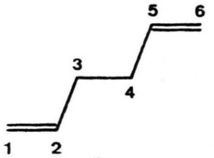
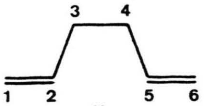
trans) are displayed below. The theoretical findings observed for the hexadiene compound are compared with results obtained for the all-trans conformation of 1,6-heptadiene (2).



1a



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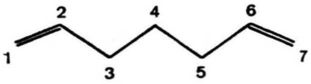

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Computational framework of this investigation is a recently designed INDO MO model [11]. Standard bondlengths and bondangles have been used for 1 and 2 [12].

2. Theory

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

$$F^{\mathrm{CMO}} = \sum_i \varepsilon_i' a_i'^{+} a_i', \quad i = 1,2,\ldots,N. \qquad (1)$$

In a subsequent step the delocalized stationary CMO's are transformed into a set of localized molecular orbitals (Equation (2)). Φ and ϱ are the colum vector of the CMO's Φ_i (3) and

$$\varrho = L \cdot \Phi \qquad (2)$$

the LMO's ϱ_i (4).

$$\Phi = \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \cdot \\ \cdot \\ \cdot \\ \Phi_N \end{pmatrix} = (\Phi_1 \Phi_2 \ldots \Phi_N)^{\mathrm{T}}, \qquad (3)$$

$$\varrho = \begin{pmatrix} \varrho_1 \\ \varrho_2 \\ \cdot \\ \cdot \\ \cdot \\ \varrho_N \end{pmatrix} = (\varrho_1 \varrho_2 \ldots \varrho_N)^{\mathrm{T}}. \qquad (4)$$

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^{CMO}, is transformed into a Fockian forming a full matrix.

$$F^{\mathrm{LMO}} = L F^{\mathrm{CMO}} L^{\mathrm{T}}, \qquad (5)$$

$$F^{\mathrm{LMO}} = \sum_i \varepsilon_i'' a_i''^{+} a_i'' + \sum_{i \neq j}\sum \varepsilon_{ij}'' a_i''^{+} a_j''. \qquad (6)$$

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

$$F_{ij}^{\mathrm{DEC}} = \sum_i \varepsilon_i'' a_i''^{+} a_i'' + \sum_{\substack{k \neq l \\ k,l \neq i,j}}\sum \varepsilon_{kl}'' a_k''^{+} a_l''. \qquad (7)$$

F_{ij}^{DEC} (7) is a full matrix with vanishing off-diagonal elements in the i'th and j'th row and column. Diagonalization of F_{ij}^{DEC} results in the eigenvectors D_{ij} of the decoupled Fockian. The back transformation (8) of F^{LMO} leads to the desired transport Fock operator F^{HT} with nonvanishing elements in the i'th and j'th row and column.

$$F^{\mathrm{HT}} = D_{ij} F^{\mathrm{LMO}} D_{ij}^{\mathrm{T}}, \qquad (8)$$

$$F^{\mathrm{HT}} = \sum_{i=i}^{j} \varepsilon_i a_i^{+} a_i + \sum_{k \neq i,j} \varepsilon_k a_k^{+} a_k + \sum_{\substack{k \\ k \neq i}} \sum_{i=i}^{j} (\varepsilon_{ki} a_k^{+} a_i + \varepsilon_{ik} a_i^{+} a_k). \qquad (9)$$

The various increments ε_i, ε_k and ε_{ki} in (9) can be rationalized in physically relevant pictures. ε_i and ε_j are the one-electron energies of the localized states ϱ_i and ϱ_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 ϱ_i and ϱ_j are removed from the potential experienced within this one-electron set. The MO basis of the $(N-2)$ k-states is symbolized by λ_k $(k = 1,2 \ldots (N-2))$.

The cross-elements $\varepsilon_{ik}/\varepsilon_{jk}$ are the interaction terms between the two localized HF states ϱ_i and ϱ_j with the remaining λ_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}.

$$\lambda^{\mathrm{HT}} = \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \cdot \\ \cdot \\ \lambda_{(N-2)} \\ \varrho_i \\ \varrho_j \end{pmatrix} = (\lambda_1 \lambda_2 \ldots \lambda_{(N-2)} \varrho_i \varrho_j)^{\mathrm{T}}. \tag{10}$$

ϱ_i and ϱ_j forming the instationary electron-hole pair are called evoluting states as these two one-electron functions are the only time-dependent ones in the selected model. To simplify the solution of the time-dependent equations the time-dependency of the $(N-2)$-dimensional subspace has been neglected forming the ensemble of messenger states. The λ_k orbitals act as transmitter functions between ϱ_i and ϱ_j via the coupling elements $\varepsilon_{ik}\,\varepsilon_{kj}$ (see below).

The separated steps for the evaluation of F^{HT} by means of eq. (5) and (8) can be combined to a single transformation-matrix M connecting F^{CMO} directly with F^{HT}.

$$M = L D_{ij}\,, \tag{11}$$

$$F^{\mathrm{HT}} = M F^{\mathrm{CMO}} M^{\mathrm{T}}. \tag{12}$$

By means of F^{HT} and λ^{HT} it is now straightforward to formulate the bais equations for the time-evolution of the selected electron-hole pair ϱ_i, ϱ_j. F^{HT} is devided into the diagonal Fockian $F^{\mathrm{HT}}_{\mathrm{D}}$ (14) associated to the λ^{HT} eigenstates and into the perturbational non-diagonal $F^{\mathrm{HT}}_{\mathrm{ND}}$ operator (15).

$$F^{\mathrm{HT}} = F^{\mathrm{HT}}_{\mathrm{D}} + F^{\mathrm{HT}}_{\mathrm{ND}}\,, \tag{13}$$

$$F^{\mathrm{HT}}_{\mathrm{D}} = \sum_{i=i}^{j} \varepsilon_i a_i^{+} a_i + \sum_{k \neq i,j} \varepsilon_k a_k^{+} a_k\,, \tag{14}$$

$$F^{\mathrm{HT}}_{\mathrm{ND}} = \sum_{\substack{k \\ k \neq i,j}} \sum_{i=i}^{j} (\varepsilon_{ki} a_k^{+} a_i + \varepsilon_{ik} a_i^{+} a_k)\,. \tag{15}$$

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

$$\lambda^{\mathrm{HT}}(t) = \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \cdot \\ \cdot \\ \lambda_{(N-2)} \\ \varrho_i(t) \\ \varrho_j(t) \end{pmatrix} = (\lambda_1 \lambda_2 \ldots \lambda_{(N-2)} \varrho_i(t)\, \varrho_j(t))^{\mathrm{T}}. \tag{16}$$

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

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

$$\varrho_i(t) = \sum_k c_k(t)\, \lambda_k\,. \tag{17}$$

The expansion (17) runs through the ϱ_i and λ_k states $(k = 1, N)$ and ε_k symbolizes the diagonal elements of the $F^{\mathrm{HT}}_{\mathrm{D}}$ operator.

In the framework of the random phase approximation (RPA) [15] the probability for the hole-propagation from ϱ_i (hole-state) to the ϱ_j electron-state is given by the squared interaction element $\langle \varrho_i | U_{\mathrm{ND}} | \varrho_j \rangle^2$, S_{ij}, where U_{ND} is the evolution operator [16] associated to the perturbational Hubbard-type Fockian $F^{\mathrm{HT}}_{\mathrm{ND}}$. U_{ND} conveniently is treated in the interaction representation (I) and is given by means of the expansion (18).

$$U_{\mathrm{ND}} = \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^{n} \int_0^{t} \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \ldots \int_0^{t'^{(n-1)}} \mathrm{d}t'^{(n)} \cdot F^{\mathrm{HT}}_{\mathrm{ND,I}}(t')\, F^{\mathrm{HT}}_{\mathrm{ND,I}}(t'') \ldots F^{\mathrm{HT}}_{\mathrm{ND,I}}(t'^{(n-1)})\,, \tag{18}$$

$$F^{\mathrm{HT}}_{\mathrm{ND,I}}(t) = U_{\mathrm{D}}^{+} F^{\mathrm{HT}}_{\mathrm{ND}} U_{\mathrm{D}} = \exp[(i|\hbar) F^{\mathrm{HT}}_{\mathrm{D}} t]\, F^{\mathrm{HT}}_{\mathrm{ND}} \cdot \exp[-(i|\hbar) F^{\mathrm{HT}}_{\mathrm{D}} t]\,. \tag{19}$$

U_{D} in (19) is the evolution operator of the diagonal $F^{\mathrm{HT}}_{\mathrm{D}}$ Fockian.

S_{ij} is obtained by means of the iterative expansion (18). An expression that is valid up to second order in perturbation is given in (20).

$$S_{ij} = S_{ij}^{(1)} + S_{ij}^{(2)}\,, \tag{20}$$

$$S_{ij}^{(1)} = \left| (i\hbar)^{-1} \int_0^{t} \mathrm{d}t' \exp(i\,\omega_{ji} t')\, \varepsilon_{ij} \right|^2, \tag{21}$$

$$S_{ij}^{(2)} = \sum_{\substack{k=1 \\ k \neq i,j}}^{N} \left| (i\hbar)^{-2} \int_0^{t} \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \cdot \exp(i\,\omega_{jk} t' + i\,\omega_{ki} t'') \cdot \varepsilon_{ik}\, \varepsilon_{kj} \right|^2, \tag{22}$$

$$\omega_{ij} = (\varepsilon_i - \varepsilon_j) | \hbar\,. \tag{23}$$

$S_{ij}^{(1)}$ is the direct transfer channel of the evoluting electron-hole pair ϱ_i and ϱ_j. It is proportional to the cross-element, ε_{ij}, between the two localized domains and depends on the Bohr frequency ω_{ij} between the initially ($t=0$) prepared hole-state (vacancy) and the electron state ϱ_j. In second order ϱ_i and ϱ_j are coupled by means of the messenger states λ_k forming $(N-2)$ indirect transfer channels in contrast to a single direct transfer path. The explicite formulas for the direct, $S_{ij}^{(1)}$, and indirect, $S_{ij}^{(2)}$, 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 instationary hole distribution (24) to the hole-distribution (25) where the vacancy ϱ_i has been filled by the donor-state ϱ_j. Obviously $c_i(t=0)$ is 0 while the donor-function ϱ_j fulfills $c_j(t=0)=1$.

$$|\lambda_1\lambda_2\ldots\varrho_i^{\text{hole}}\varrho_j^{\text{donor}}|\,, \tag{24}$$

$$c_i(t)=0\,,\quad c_j(t)=1\,,\quad t=\sigma\,,$$

$$|\lambda_1\lambda_2\ldots\varrho_i^{\text{donor}}\varrho_j^{\text{hole}}|\,, \tag{25}$$

$$c_i(t')=1\,,\quad c_j(t')=\sigma\,,$$

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

In (26) the time of hole-equibrilation among the ϱ_i/ϱ_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] sucessfully applied in the transition state theory within the X_α 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 ϱ_j are dynamically coupled by means of the relations (27) and (28) which obey the rules of conservation of energy:

$$\varepsilon_i(t_n)=\varepsilon_i(t_{n-1})+(1-S_{ij}(t_{n-1}))\cdot\Delta_i\,, \tag{27}$$

$$\varepsilon_j(t_n)=\varepsilon_i(t_{n-1})+S_{ij}(t_{n-1})\cdot\Delta_i\,. \tag{28}$$

$\varepsilon_i(t_n)$ and $\varepsilon_j(t_n)$ 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, Δ_i is the reorganizational correction in the limit of full hole-localization. The determination of Δ_i for decoupled bonds, lone-pairs or metal d orbitals is described in [9]. The dynamic coupling between ϱ_i and ϱ_j is clearly recognized in (27) and (28). At $t=0\,S_{ij}(0)=0$ 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 ε_i in the hole-state ϱ_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 ε_{ij}, ε_{ik} and ε_{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 π orbitals in five conformations. In the case of the two extreme trans-trans (**1a**) and cis-trans (**1b**) conformation only two CH-σ orbitals (see Fig. 1) can act as messenger states for the transfer of the π vacancy. In the conformations with a torsional angle $\alpha=$ 135°, 90° and 45° between both π moieties the hole-transfer additionally can be submitted also via

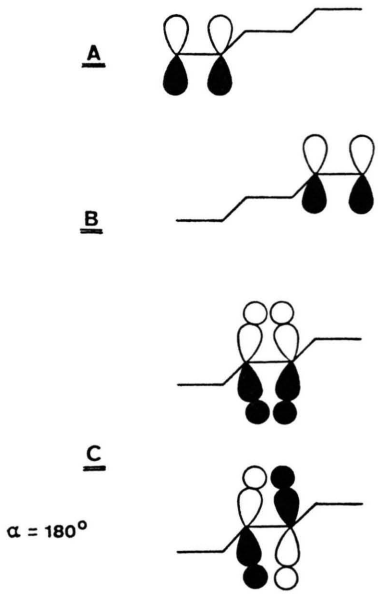

Fig. 1. Localized electron-(ϱ_j) (**A**) and hole-(ϱ_i) (**B**) states as well as the available CH-σ messenger orbitals (**C**) in trans-trans 1,5-hexadiene **1a**.

Table 1. Localized molecular orbitals of 1,5-hexadiene in the 90° conformation.

MO-Type	Number	$\varepsilon_i^{\mathrm{LMO}}$ (eV)	Impurities %
CC-σ			
$C_1C_2{=}C_5C_6$	2	– 22.53	0.04
$C_2C_3{=}C_4C_5$	2	– 21.83	0.23
C_3C_4	1	– 20.43	0.08
CH-σ			
$C_2H_3{=}C_5H_8$	2	– 20.83	0.30
$C_1H_1{=}C_6H_9$	2	– 20.60	0.28
$C_1H_2{=}C_6H_{10}$	2	– 20.47	0.24
$C_3H_4{=}C_3H_5{=}$ $C_4H_6{=}C_4H_7$	4	– 20.25	0.68
CC-π			
$C_1C_2{=}C_5C_6$	2	– 11.57	0.09

CC-σ linearcombinations. Furthermore the direct transfer channel must be taken into account.

To demonstrate the general computational method we have collected the localized molecular orbitals of the 90° conformation of 1,5-hexadiene in Table 1. The intrinsic Edmistion-Ruedenberg localization leads to five CC-σ orbitals, to ten localized CH-σ combinations and to the two π orbitals forming the electron-hole pair for the intramolecular transfer. The transformed one-electron states representing the basis of the F^{HT} operator are summarized in Table 2. The diagonal elements ($F_{\mathrm{D}}^{\mathrm{HT}}$) as well as the tunneling increments (ε_{ik}, ε_{jk}, ε_{ij}) of the perturbational operator $F_{\mathrm{ND}}^{\mathrm{HT}}$ are given in column 4, 5 and 6. The MO's of the λ_k set (MO 1 — MO 15) transform according to the irreducible representations of the C_2 pointgroup. MO 16 and MO 17 are the two instationary localized π-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 λ_k states correspond to the various CH-σ linearcombinations.

In Tables 3 and 4 we have collected characteristic quantities for the transfer dynamics in 1,5-hexadiene for torsional angles of 180°, 135°,

Table 2. One-electron states ϱ_i, ϱ_j and λ_k ($k \neq i, j$) of the transfer Fockian F^{HT} of 1,5-hexadiene in the 90° conformation. The irreducible representations (Γ_k) of the λ_k states under C_2 symmetry, the diagonal and off-diagonal elements of F^{HT} (in eV) as well as the type of the one-electron states are also given.

MO Nr.	Γ_k	MO-Type	ε_k	ε_{ik}	ε_{jk}	% C	% H
1	1a	CC-σ	– 41.60	– 0.08	– 0.08	79.8	20.2
2	1b	CC-σ	– 35.80	– 0.27	0.27	82.4	17.6
3	2a	CC-σ	– 31.12	0.10	0.10	77.6	22.4
4	2b	CH-σ	– 25.32	– 0.20	0.20	64.2	35.8
5	3b	CH-σ	– 23.18	– 0.67	0.67	63.8	36.2
6	3a	CH-σ	– 22.99	– 0.56	– 0.56	61.1	38.9
7	4a	CH-σ	– 18.37	0.37	0.37	70.7	29.3
8	4b	CH-σ	– 17.65	0.74	– 0.74	65.5	34.5
9	5a	CC-σ	– 17.12	– 0.76	– 0.76	73.3	26.7
10	5b	CH-σ	– 15.68	0.52	– 0.52	65.8	34.2
11	6a	CH-σ	– 13.92	– 0.57	– 0.57	60.0	40.0
12	6b	CH-σ	– 13.69	0.59	– 0.59	68.1	31.9
13	7a	CH-σ	– 12.87	0.13	0.13	69.8	30.2
14	7b	CH-σ	– 12.51	– 0.29	0.29	70.5	29.5
15	8a	CC-σ	– 12.20	– 0.21	– 0.21	86.3	13.7
16	loc	$\varrho_i(\pi\text{-}C_1C_2)$	– 11.57	—	– 0.11	100.0	0.0
17	loc	$\varrho_j(\pi\text{-}C_5C_6)$	– 11.57	– 0.11	—	100.0	0.0

Table 3. Times of localization in 1,5-hexadine (**1**) of an initially prepared hole-state at ϱ_i. $T_{c.25}$ and $T_{c.50}$ represent the times necessary that 25% and 50% of the i'th hole-state has been transfered to the j'th electron state. The $T_{c.n}$ values have been obtained in the framework of an independent electron model.

α [°]	$T_{c.25}$ (sec)	$T_{c.50}$ (sec)
180	6.31×10^{-16}	8.95×10^{-16}
135	7.72×10^{-16}	9.60×10^{-16}
90	1.00×10^{-15}	1.36×10^{-15}
45	8.83×10^{-16}	1.13×10^{-15}
0	5.27×10^{-16}	7.45×10^{-16}

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

α [°]	$T_{c.25}$ (sec)	$T_{c.50}$ (sec)
180	7.04×10^{-16}	8.66×10^{-16}
135	8.10×10^{-16}	1.01×10^{-15}
90	1.10×10^{-15}	1.64×10^{-15}
45	9.39×10^{-15}	1.26×10^{-15}
0	6.12×10^{-16}	7.72×10^{-16}

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 ϱ_i (hole-state)$\rightarrow\varrho_j$ (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 equibrilation of the initially prepared ϱ_i hole-state within the evoluting ϱ_i, ϱ_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 Δ_i within ϱ_i and ϱ_j. It is seen that the Δ_i 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 electronical 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 π-system (e.g. benzene) by about a power of ten (0.8—2.4×10^{-16} sec) [23].

To rationalize the α-dependent $T_{c.n}$ values we have collected the contributions from the individual transfer channels (direct and indirect via the λ_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 α (180°, 135°, 90°, 45° and 0°). In the case of $\alpha = 180°$

Table 5. Transfer channels in the 180° conformation (**1a**) of 1,5-hexadiene.

Transfer channel MO Nr. + Type		Contribution %
7	CH-σ	40.26
12	CH-σ	59.71
direct	CC-π	0.03

Table 6. Transfer channels of **1** in the 135° conformation.

Transfer channel MO Nr. + Type		Contribution %
6	CH-σ	0.26
7	CH-σ	5.29
8	CH-σ	5.97
9	CH-σ	0.10
10	CC-σ	1.20
11	CH-σ	3.56
12	CH-σ	82.93
15	CC-σ	0.26
direct	CC-π	0.43

Table 7. Transfer channels of **1** in the 90° conformation.

Transfer channel MO Nr. + Type		Contribution %
5	CH-σ	1.36
6	CH-σ	0.68
7	CH-σ	0.29
8	CH-σ	6.77
9	CC-σ	10.73
10	CH-σ	3.25
11	CH-σ	23.93
12	CH-σ	35.34
13	CH-σ	0.20
14	CH-σ	5.34
15	CC-σ	1.74
direct	CC-π	10.37

Table 8. Transfer channels of **1** in the 45° conformation.

Transfer channel MO Nr. + Type		Contribution %
5	CH-σ	0.89
6	CH-σ	5.57
8	CH-σ	19.81
9	CC-σ	0.91
10	CH-σ	0.55
11	CH-σ	35.15
13	CH-σ	29.70
14	CC-σ	0.10
15	CH-σ	3.89
direct	CC-π	3.43

Table 9. Transfer channels in the 0° conformation (**1b**) of 1,5-hexadiene.

Transfer channel MO Nr. + Type		Contribution %
8	CH-σ	22.15
12	CH-σ	69.92
direct		7.93

and α = 0° 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-σ linearcombination (MO 12).

For α = 135°, 90° and 45° additional CH-σ and CC-σ channels are opened for the intramolecular hole-transport. In Table 6 it is seen that predominantly one messenger state (MO 12, CH-σ) 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 ϱ_i and ϱ_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 π-domains with perpendicular orientation here exceeds the "through space" coupling encountered in the various other geometries (see Figure 2).

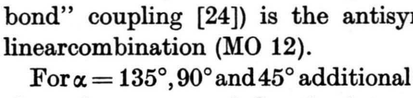

Fig. 2. Orientation of the electron-hole pair ϱ_j, ϱ_i in the 90° conformation of 1,5-hexadiene.

Table 10. The contribution of the varions transfer channels (CH-σ, CC-σ and direct) to the net transfer probability in **1** as function of the torsional angle.

α [°]	Transfer channels		
	CH-σ %	CC-σ %	direct %
180	99.97	0.00	0.03
135	98.21	1.36	0.43
90	77.16	12.47	10.37
45	95.56	1.01	3.43
0	92.07	0.00	7.93

In Table 10 we have summarized the contributions of the three transfer types (direct, indirect via CH-σ channels and indirect via CC-σ channels) of **1** in the different molecular conformations. It is seen that CC-σ messenger states only contribute to the transfer process in the 90° system while the CC-σ 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 $T_{c.n}$ parameters for α = 90° thus are the result of a reduction of the available CH-σ channels and a magnification of the less efficient CC-σ transmitter paths. In Table 2 it is shown that the coupling terms between CC-σ and ϱ_i, ϱ_j are smaller than the tunnel elements of the localized states to the CH-σ messenger set.

In the all-trans conformation **2** of 1,6-heptadiene the central C atoms of the two π orbitals are separated by 3.86 Å. Three symmetry adapted CH-σ messenger orbitals allow the intramolecular hole-transport. According to the theoretical approach $T_{c.25}$ and $T_{c.50}$ values of 7.18×10^{-16} sec (6.72×10^{-16} sec) and 1.02×10^{-15} sec (1.13×10^{-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 satured C-center chain separating the π-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

Transfer channel MO Nr. + Type		Contribution %
8	CH-σ	12.44
12	CH-σ	73.57
14	CH-σ	13.98
direct		<0.01

Table 11. Transfer channels in the all-trans conformation of 1,6-heptadiene.

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 λ_{12} where large cross-elements (see Fig. 3) and small Bohr frequencies both allow an efficient "through bond" coupling for the evoluting electron-hole pair. As result of the smaller LCAO amplitudes at C_3 and C_5 within the two symmetrical CH-σ combinations, λ_8 and λ_{14}, the transfer channels via these states are less important.

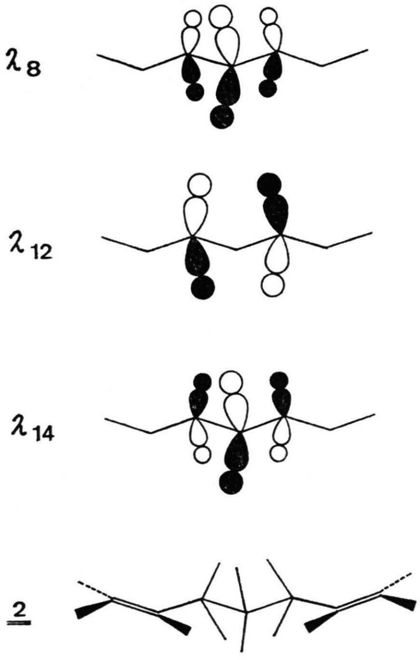

Fig. 3. The available CH-σ messenger states in the all-trans conformation of 1,6-heptadiene **2**.

4. Conclusions

It has been demonstrated that the delocalization of hole-states or vacancies in nonconjugated π-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 π-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 $T_{c.n}$ parameters of about 10^{-15} sec should be compared with localization times of 10^{-16} sec in conjugated π-systems [23] 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 evoluting states and the ligand one-electron set leads to slower transfer rates.

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