The Determination of Molecular Quantities from Measurements on Macroscopic Systems

V. Existence and Properties of 1:1 and 2:1-Electron-Donor-Acceptor Complexes of Hexamethylbenzene with Tetracyanoethylene

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The formation of electron-donor-acceptor complexes of hexamethylbenzene (HMB) with tetracyanoethylene (TCNE) was investigated by measurements of the optical absorptions, the densities, the permittivities and the electro-optical absorptions of solutions in CO₂. The careful evaluation of data based on some previously reported models, has shown that the assumption of the formation of the 1:1 and the 2:1 complex agrees with all experimental data, but that the assumption of the formation of only the 1:1 complex is contradictory to experimental facts even if the activity effects on the equilibrium constant and of the solvent dependences of observed molar quantities are taken into account. The evaluation leads to the molar optical absorption coefficients and the molar volumes of both complexes and to their electric dipole moments in the electronic ground state and the considered excited state. According to these results the complexes are of the sandwich type HMB-TCNE and HMB-TCNE-HMB. In spite of the fact that the 2:1 complex owns a center of symmetry, at least approximately, there is a rather large electric dipole moment in its excited state. Furthermore, values for the equilibrium constants and for the standard reaction enthalpies of both complex formation reactions are estimated from experimental data.

1. Introduction

Electron-donor-acceptor (EDA) complexes with a stoichiometric composition different from 1:1 have been observed in the solid state already a long time ago [1], they have been discussed by Mulliken [2]. The evidence of the existence of EDA complexes in solutions is mostly based on optical absorption measurements of solutions of donor and acceptor molecules with varying concentrations. For the evaluation of such data it is usually assumed that there exists a complex with the stoichiometric composition 1:1. In some such investigations it was observed that the equilibrium constant determined for the assumed 1:1 complex apparently depends on the wavenumber used for the absorption [3—8] or on the interval of concentrations of donors and acceptors [3—5, 9]. Furthermore, equilibrium constants determined by other methods as NMR measurements [10, 11], equilibrium ultracentrifugation [12] or the partition method [13, 14] did not agree with those from optical absorption measurements. Such apparent anomalies could be explained assuming the formation of 2:1-EDA complexes besides the well known 1:1 complex [3], as was done in the case of the hexamethylbenzene-tetracyanoethylene complexes, for example [12, 15]. According to these measurements the 2:1 complex has an absorption band at nearly the same wavenumber interval as the 1:1 complex, with both complexes solvated in cyclohexane. Dielectric measurements of Brriegleb, Czekalla and Reuß [16] have been evaluated by Foster and Kulevsky [17] using the equilibrium constants determined from optical absorption measurements. This procedure leads to an electric dipole moment for the 1:1 complex and a vanishing one for the 2:1 complex. Hence one has to assume that the complex is at least nearly of sandwich type D-A-D, and not D-D-A, as was proposed for an exciplex [18]. Because of these results the assumption of the existence of the 2:1 complex besides the 1:1 complex seems to be dubious for the following reason: the absorption bands of weak-bond 1:1 and corresponding 2:1 complexes in the gaseous phase are expected in nearly the same wavenumber intervals. In the 1:1 complex the electric dipole moment in the excited charge-transfer state corresponding to the EDA band is increased relative to the dipole moment in the ground state, and this should cause a red shift of the band of the solute...
molecule of approximately $1 \cdot 10^5$ m$^{-1}$, additive to
the red shift caused by dispersion interactions be-
tween the complex molecule and the surrounding
solvent molecules. If the corresponding 2:1 com-
plex is of the sandwich type, one should expect a
(nearly) vanishing dipole moment in the excited
state as well as in the ground state. This should cause
a blue shift of the absorption band of the 2:1 com-
plex relative to the 1:1 complex of approximately
$1 \cdot 10^5$ m$^{-1}$, contrary to the experimental result.

Other authors tried to explain the above described
apparent anomalies by other reasons; for example,
association of the donor, acceptor or complex mole-
ecule with the solvent [19—26], self-association of
a complex relative to the 1:1 complex of approximately
a blue shift of the absorption band of the 2:1 com-
plex is of the sandwich type, one should expect a
solvent molecules. If the corresponding 2:1 com-
plex relative to the 1:1 complex of approximately

The aim of our investigation was to decide, if
possible, between the different interpretations of the
apparent anomalies; similar studies have been done
by Scott [24, 29], Hayman [33], Hanna and Rose
[30], Deranleau [34], and Kreysig et al. [35]. All
research on chemical equilibrium reactions is based
on data obtained from measurements on macro-
scopic phases and is intimately related to the prob-
lem of the determination of molecular quantities
from such measurements. In paper I of this series
we investigated the relations between bulk quan-
tities, which can be measured on macroscopic sys-
tems, and molecular quantities, which have to be
introduced by some theoretical model [36]. In pa-
per II permittivity measurements and in III electro-
optical absorption measurements have been treated
as examples [37, 38]. In paper IV the method was
extended to phases where chemical reactions occur
[39]. These results are applied in this paper to solve
the problems described above.

2. The System, the Models and the Evaluation
of Data

2.1. The Investigated System and the Determined
Bulk Quantities

The interactions of the electron donor hexa-
methylbenzene (HMB, $A_2$) with the electron accep-
tor tetracyanoethylene (TCNE, $A_3$) have been in-
vestigated repeatedly [5, 12, 15—17, 23, 40—45].
The solvent chosen in our studies was carbon tetra-
chloride ($A_1$), because its molecules own neither an
electric dipole moment nor a quadrupole moment
and hence this solvent is very suited for permittiv-
ty and electro-optical absorption measurements;
Furthermore, in carbon tetrachloride the maximal
solubility of the acceptor $A_3$ (approximately
$(c_{03})_{\text{max}} = 0.5$ mol m$^{-3}$) is much larger than in ali-
phatic hydrocarbons, and the maximal solubility of the donor $A_2$ (approximately $(c_{02})_{\text{max}} = 750$
 mol m$^{-3}$) is also rather large.

Measured were the mass densities $\rho$, the optical
absorption coefficients $\alpha$, the relative permittivities
$\varepsilon_r$, the refractive indices $n$ and the derivatives

$$M = \lim_{E_0 \to 0} (\partial \alpha / \partial E_0 \alpha^2),$$

where $E_0$ is the magnitude of an applied electric
field, of solutions with known mass fractions $w_{02}$
and $w_{03}$ of HMB and TCNE, respectively. From
these data the generalized densities $P_{w\varphi}$, defined by
Eq. (I.57)*, which are equal to the corresponding
specific quantities if mass fractions are chosen as
concentration variables, can be determined, namely

$$P_{w\varphi} = 1/\rho, \quad P_{wK} = \alpha / \rho, \quad P_{wZ} = (\varepsilon_r - 1) / \rho, \quad P_{wY} = M / \rho.$$  

The corresponding PMQ's are assumed to be of
class $Aa$ [36], which is confirmed by the obtained
results. Therefore the specific quantities satisfy
(I.63) or

$$P_{w\Phi} = P_{w\Phi}^+ + (M_3^{-1} \Phi_{03}^+ - P_{w\Phi}^+) w_{03}$$
$$+ [M_3^{-1} A_{w\Phi 12}^+ (1 - w_{02}^2)$$
$$+ M_5^{-1} A_{w\Phi 22}^+ w_{02}^2$$
$$+ M_3^{-1} A_{w\Phi 31}^+ w_{03}^2 + \ldots],$$

where $M_1$, $M_2$ and $M_3$ are the molar masses of $A_1$
$A_2$ and $A_3$, respectively, and $\Phi_{03} = (\partial \Phi / \partial (n_{03} m_0))_{m_0}$, $\Phi_{03}$
is the partial molar quantity of the substance $A_3$
adjoint to the extensive quantity $\Phi = P_{w\Phi} m_0$ as
defined by (I.22); $m_0$ is the total mass of the solution.
A quantity with a cross as a superscript is the limit
of this quantity for vanishing concentration of $A_3$.

* The abbreviations Eq. (I,...),..., (IV,...) signify equa-
tions of paper I,..., IV of this series [36—39].
The quantities \( A_{\Phi j,a} \) are the coefficients of the expansion
\[
\Phi_{0j} = \Phi_{0j}^+ + \sum_{a=1}^{\infty} A_{\Phi j,a} w_{03}^a,
\]
as defined by (I.40), (I.46) and (I.47).

From a set of data \( D_{wp} = \{(P_{wp}, w_{03}; w_{02}^i)\} \) with a fixed value of \( w_{02}^i \), the number of coefficients in (1) significantly different from zero can be determined by analysis of variance (F- and t-test). Multiple regression according to (1) then leads to estimators for \( \Phi_{0p}^+ \) and \( \Phi_{03}^+ \) and possibly a few further coefficients of the power-series expansion in \( w_{03} \). The analysis of the available data has shown that in the investigated concentration intervals all considered specific quantities are only linearly dependent on \( w_{03} \). Hence values for the limits \( \Phi_{0p}^+ \) and \( \Phi_{03}^+ \) can be estimated and all further coefficients \( A_{\Phi j,a} \) have to be assumed negligibly small. The partial molar quantities \( \Phi_{03}^+ \) of TCNE and their dependence on \( w_{02}^+ \) embrace all information available about chemical reactions and model molar quantities of the corresponding products, as will be shown in the following sections.

2.2. The Model for the Occurring Chemical Reactions

Neither the association of the donor, acceptor or complex molecules with solvent molecules nor the existence of different molecules with equal stoichiometrical composition can be the reason for the apparent anomalous behaviour of the solutions of hexamethylbenzene and tetracyanoethylene as has been shown in Sect. 6 of paper IV [39]. If such reactions occur, they cannot be recognized from (IV.64) and (IV.75), for example. The same holds true in case of contact-charge-transfer interactions, where any contact configuration of two or more molecules can be considered as a species with equal stoichiometrical composition as the corresponding complex.

The following chemical reactions are assumed to be possible:
\[
\lambda A_2 + v A_3 \rightleftharpoons A_{\lambda v},
\]
\[
\lambda = 0, 1, 2, \ldots; \quad v = 0, 1, 2, \ldots; \quad \lambda = v \pm 0,
\]
\[
\lambda = v - 1 \pm 0, \quad \lambda = v \mp 0.
\]
The totality of these reactions constitutes the hypothesis of occurring chemical reactions. Included are all possible associations between donor and acceptor molecules (\( \lambda \neq 0 \) and \( v \neq 0 \)) as well as associations of donor molecules among themselves (\( \lambda \geq 2, v = 0 \)) and of acceptor molecules among themselves (\( \lambda = 0, v \geq 2 \)). Equation (3) corresponds to (IV.1) with \( R = \lambda v, r_{R2} = -\lambda, r_{R3} = -v \) and \( r_{RJ} = 1 \) for \( J \geq 4 \). From the results of the evaluation it will be shown that all available data can be explained with two reactions of the type (3), i.e. formation of the 1:1 EDA complex (\( \lambda = 1, v = 1 \)) and of the 2:1 complex (\( \lambda = 2, v = 1 \)).

2.3. Equilibrium Constants, Model Molar Quantities and the Evaluation of Data

The equilibrium constants \( K_{wp}^* \) corresponding to the hypothetical chemical reactions (3) are related to the quantities \( K_{wp} \) according to (IV.32) and (IV.36) as
\[
K_{wp}^*= (1 + F_{wp}) = \frac{\psi_{wp}^{\pm}}{\frac{1}{2} \psi_{3}^{\mp}} (\psi^\oplus)^{4+v-1},
\]
where \( \psi_{wp}^{\pm} \) is the value of the concentration variable of substance \( A_J \) (\( J = 2, 3, \lambda v \)) in the equilibrium state as defined by (I.72):
\[
\psi_{wp} = n_J / X_J \Psi.
\]
\( n_J \) is the amount of the substance \( A_J \) present in the solution, \( \Psi \) is an extensive quantity and \( X_J \) a constant, possibly different for different substances \( A_J \); examples are listed in Table 1 of the first paper [36]. \( \psi^\oplus \) is a standard quantity with an arbitrary value and a unit equal to the one of \( \psi_{wp}^{\pm} \). The quantity \( F_{wp} \) as defined by (IV.34) describes the activity effects. It is related to the activity coefficients \( f_{wp}^{\pm} \), defined by (I.132) and (I.133), as
\[
F_{wp} = \frac{f_{wp}^{\pm}}{f_{wp}^{\pm}} - 1.
\]
According to (IV.39) a power-series expansion in \( \psi_{02} \) and \( \psi_{03} \) is possible:
\[
F_{wp} = \eta \psi_{wp}^{10} \psi_{02} + \eta \psi_{wp}^{01} \psi_{03} + \eta \psi_{wp}^{11} \psi_{02} \psi_{03} + \cdots,
\]
such that \( \lim F_{v\lambda r} = 0 \), where \( n_0 = n_{01} + n_{02} + n_{03} \) and \( n_{0j} \) is the initial amount of the pure substance \( \lambda_j \) used to generate the solution. The \( \psi_j \)'s are related to the concentration variables \( \psi_{0j} \),

\[
\psi_{0j} = n_{0j}/\chi_j, \tag{8}
\]

by (IV.6), or, specialized for the considered case:

\[
\psi_2 = \psi_0 - \chi_2^{-1} \sum_{\lambda} \chi_2 \xi_{v\lambda r},
\]

\[
\psi_3 = \psi_0 - \chi_3^{-1} \sum_{\lambda} \chi_3 \xi_{v\lambda r},
\]

\[
\psi_{v\lambda r} = \chi_1^{-1} \xi_{v\lambda r},
\]

where \( \xi_{v\lambda r} \), as defined by (IV.5), is the extent of the reaction (3) in a unit equal to that of \( \chi_1 \psi_{01} \).

Any generalized density \( P_{v\phi} = P_{v\phi} n_{00}/\Psi \) is related to the corresponding model molar quantities \( \varphi_j \) (MMQ's) according to (IV.11) as

\[
P_{v\phi} = \frac{1}{3} \sum_{\lambda} \chi_1 \psi_{01} \varphi_j + \sum_{\lambda} \xi_{v\lambda r} A_{\lambda v} \varphi_j,
\]

where, as defined by (IV.12),

\[
A_{\lambda v} \varphi = \varphi_{\lambda v} - \lambda \varphi_{2v} - \nu \varphi_3.
\]

The dependence of any \( q_j \) on the composition of the phase can be represented by power-series expansion in \( \psi_{02} \) and \( \psi_{03} \) as introduced in (1.84), or

\[
q_j = q_j^* + \lambda q_j \varphi_{01} \psi_{02} + \lambda q_j \varphi_{02} \psi_{03} + \cdots,
\]

\[
J = 1, 2, 3 \text{ or } \lambda v,
\]

and similarly

\[
A_{\lambda v} \varphi = A_{\lambda v} \varphi^* + A_{\lambda v} \varphi_{01} \psi_{02} + A_{\lambda v} \varphi_{02} \psi_{03} + \cdots.
\]

The MMQ's \( q_j \) are related to the PMQ's \( \Phi_{0j} \) as shown in (IV.14), or

\[
\Phi_{03} = \varphi_3 + \frac{1}{3} \sum_{\lambda} \chi_1 \psi_{01} \varphi_j + \frac{1}{3} \sum_{\lambda} \xi_{v\lambda r} A_{\lambda v} \varphi_j + \frac{1}{3} \sum_{\lambda} \sum_{\lambda'} \left( \frac{\partial (\xi_{v\lambda r} A_{\lambda v} \varphi)}{\partial \psi_{01}^{\lambda} \lambda} \right)_{\psi_{02}^{\lambda}, \varphi_{01}^{\lambda}} + \frac{1}{3} \sum_{\lambda} \sum_{\lambda'} \left( \frac{\partial (\xi_{v\lambda r} A_{\lambda v} \varphi)}{\partial \psi_{03}^{\lambda} \lambda} \right)_{\psi_{02}^{\lambda}, \varphi_{01}^{\lambda}}.
\]

According to (1.18) and (1.19), the following relation holds true:

\[
\left( \frac{\partial \gamma}{\partial \psi_{01}} \right)_{\psi_{02}} = \left( \frac{\partial \gamma}{\partial \psi_{03}} \right)_{\psi_{02}} = \chi_3 \left( \frac{\varphi_{01}^*}{\varphi_{02}^*} \right) \frac{\varphi_{01}^*}{\varphi_{02}^*} \left( \frac{\varphi_{01}^*}{\varphi_{02}^*} \right)_{\psi_{02}}.
\]

Introducing (18) and the limits of the different quantities as obtained from the given equations into (17) leads, after some lengthy calculations to

\[
\Phi_{03} = -B_{\phi 0} + B_{v\phi 1} \psi_{02} + B_{v\phi 2} (\psi_{02})^2 + \cdots
\]

\[
1 + A_{\psi 1} \psi_{02} + A_{\psi 2} (\psi_{02})^2 + \cdots,
\]

where

\[
A_{\psi 1} \psi_1 = \chi_3^{-1} \chi_{11} K_{\psi_{11}}^*,
\]

\[
A_{\psi 2} (\psi_{02})^2 = \chi_3^{-1} \left\{ \chi_{11} K_{\psi_{21}}^* + \chi_{11} K_{\psi_{11}}^* \right\} (\psi_{01})^2 - 2 \chi_2^{-1} \chi_0 K_{\psi_{20}}^*,
\]

\[
B_{\phi 0} = B_{\psi 1} \psi_{02} + B_{\psi 2} (\psi_{02})^2 + \cdots
\]

\[
B_{v\phi 1} = A_{\psi 1} (\psi_{02})^2 + \chi_3^{-1} \psi_{01}^* \psi_{01}^* + A_{\psi 4} (\psi_{02})^2 + \cdots
\]

\[
1 - \chi_3^{-1} \psi_{01}^* \chi_2 \psi_{02}^* \lambda \psi_{01}^* + C_1 - \chi_3^{-1} \psi_{01}^* \psi_{02}^* \lambda \psi_{01}^*.
\]
The further coefficients $B_{\psi\varphi_3}$, $B_{\psi\varphi_4}, \ldots$ and $A_{\psi_3}$, $A_{\psi_4}, \ldots$ in (19), which can be calculated similarly, are not listed explicitly since they are not needed in the following studies. A quantity with a star as a superscript is the limit of this quantity for vanishing concentrations of HMB (and TCNE), i.e. for $\psi_0 \to 0 (\psi_3 \to 0)$ with a fixed value of $n_0$. The quantity $B_{\psi_0}$ is equal to the limit $\Phi_{\psi_3}$ of the corresponding partial molar quantity of substance $A_3$. An equation similar to (19) but for a somewhat simplified case was discussed by Deranleau [34]. For the case $A_{\psi_1} \psi_{02} + A_{\psi_2} (\psi_0^\varphi)^2 + \cdots \leq 1$, i.e. at sufficiently low concentrations $\psi_{02}$, a series expansion of the denominator of (19) leads to an equation similar to a series expansion discussed by Hayman [33]. Under such a condition any evaluation assuming the formation of only a 1:1 complex may be satisfied but the apparent value of the equilibrium constant is actually related to the value of $A_{\psi_1} - B_{\psi_{01}}/B_{\psi_{01}}$ as was recognized by Hayman [33]. Since $B_{\psi_{02}}/B_{\psi_{01}}$ may be different for different specific quantities $P_{\psi\varphi}$, the apparent value of the equilibrium constant may be different when different measurements are taken (different wavenumbers at optical absorption measurements, for example). A separate determination of the coefficients $A_{\psi_1}$ and $B_{\psi_{02}}$ is possible only if for some of the investigated solutions $A_{\psi_1} \psi_{02}$ is comparable or even larger than one [46], when the series expansion of the denominator of (19) is not possible any more. Under such a condition the evaluation of sets of data $\{(\Phi_{\psi_3}, \psi_{02}^\varphi)\}$ according to (19) may lead to estimators for $A_{\psi_1}, A_{\psi_2}, \ldots, B_{\varphi_0}, B_{\psi_01}, B_{\psi_{02}}, \ldots$, as will be shown in Section 4.1.

Equations (20) and (21) show that only the equilibrium constant $K_{\psi_1}^*$ for the formation of the 1:1 complex HMB-TCNE can uniquely be determined if $A_{\psi_1}$ is different from zero. A value of $A_{\psi_2}$ different from zero can be caused by the formation of the 2:1 complex (HMB)$_2$-TCNE as well as by $n_{\psi_1,1,10}$, describing an activity effect on the formation of the 1:1 complex in first order, or by the formation of the dimere (HMB)$_2$. But at least in the latter case it has to be $A_{\psi_2} < 0$. Neither the obtained value of $A_{\psi_2}$ (compare Sect. 4.1), which is larger than zero, nor any other experimental data give a clue about the dimerisation of the donor molecule HMB in the solvent CCl$_4$. Hence we assume $K_{\psi_2}^* = 0$.

A further evaluation of the quantities $B_{\psi\varphi_3}$ can lead to the MMQ's $\varphi_{11}^*$ and $\varphi_{21}^*$ of the 1:1 and 2:1 complexes, respectively, as can be recognized from (23) and (24). For that purpose not only the values of $A_{\psi_1}$ and $A_{\psi_2}$ have to be known but also the values of $\varphi_{2}^*$ and $\varphi_{3}^*$ and of the coefficients $\lambda_{\psi_2 J_{233}}$ as introduced in (14). The quantities $\varphi_{2}^*$ and $\varphi_{3}^*$ can be obtained from measurements of solutions of only one substance $A_2$ or $A_3$, respectively, in the same solvent as has been discussed in paper I [36]; $\varphi_{3}^*$ can also follow from $B_{\varphi_0}$. The quantities $\lambda_{\psi_2 J_{233}}$ have to be represented on the basis of some appropriate molecular model, as has been outlined previously [36-38].

3. Experimental Details

Tetracyanoethylene (TCNE) was purified by repeated recrystallisation in chlorobenzene and vacuum sublimation, hexamethylbenzene (HMB) by repeated recrystallisation in cyclohexane and zone melting. Carbon tetrachloride was washed with NaOH, H$_2$O, dried with CaCl$_2$ and P$_2$O$_5$, fractioned over a column with aluminium oxide in the dark.

Density measurements were made with the device DMA 02 (Paar KG, Graz), optical absorption measurements with a spectrophotometer PMQ 2 with double monochromator MM 12 (Zeiss, Oberkochen).
permittivity measurements with the device DM01 (WTW, Weilheim), refractometric measurements with a differential refractometer [47]. The device for the electro-optical absorption measurements has been described previously [48].

4. Evaluation and Results

4.1. Optical Absorption Measurements

The absorption coefficients \( a \) of several sets of solutions with fixed values of the mass fraction \( \nu_0^+ \) of HMB were measured, each set consisting of a few solutions with variable values of the mass fraction \( \nu_0 \) of TCNE \( (c_0^+ \approx 7 \text{ to } 700 \text{ mol m}^{-3}, c_0^0 \approx 0.1 \text{ to } 1 \text{ mol m}^{-3}). \) Analysis of variance (F- and t-test) of the data has shown that in the investigated concentration intervals the specific quantity \( P_{\text{eK}} = a/\varrho \), where \( \varrho \) is the density of the solution, is linearly dependent on the mass fraction \( \nu_0 \) and that in the investigated wavenumber interval \( \tilde{v} = 15 \cdot 10^5 \text{ to } 25 \cdot 10^5 \text{ m}^{-1}, \) the limit of \( P_{\text{eK}} \) for \( \nu_0 \to 0 \) vanishes.

<table>
<thead>
<tr>
<th>( \tilde{v} \cdot 10^5 \text{ m}^{-1} )</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_0^0 ) mol m(^{-3} )</td>
<td>7.7372</td>
<td>30.413</td>
<td>30.721</td>
<td>53.033</td>
<td>129.79</td>
<td>339.53</td>
</tr>
<tr>
<td>( K^+_{03} \text{ m}^2 \text{ mol}^{-1} )</td>
<td>191.5</td>
<td>398.3</td>
<td>399.6</td>
<td>484.1</td>
<td>591.0</td>
<td>622.0</td>
</tr>
</tbody>
</table>

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Table 1. Values of the limit \( K_{03}^+ \) of the partial molar absorption of TCNE for solutions of HMB and TCNE in CC1\(_4\) at 298.15 K.

\[
\tilde{v} = 15 \cdot 10^5 \text{ to } 25 \cdot 10^5 \text{ m}^{-1},
\]

\[
\begin{array}{c|c|c|c|c|c|c}
\hline
\tilde{v} \cdot 10^5 \text{ m}^{-1} & 17 & 18 & 19 & 20 & 21 & 22 \\
\hline
7.7372 & 191.5 & 247.7 & 257.1 & 225.1 & 166.0 & 105.3 \\
30.413 & 398.3 & 399.6 & 484.1 & 591.0 & 622.0 & 262.0 \\
30.721 & 53.033 & 129.79 & 339.53 & 654.65 & 256.9 & 151.9 \\
53.033 & 129.79 & 405.1 & 520.5 & 528.0 & 453.5 & 335.9 \\
129.79 & 405.1 & 520.5 & 528.0 & 453.5 & 335.9 & 217.3 \\
270.14 & 448.4 & 574.8 & 577.5 & 491.7 & 389.3 & 255.2 \\
339.53 & 460.7 & 590.1 & 591.1 & 502.1 & 389.3 & 255.2 \\
589.28 & 486.4 & 622.0 & 619.6 & 523.7 & 392.0 & 256.9 \\
654.65 & 490.0 & 626.8 & 624.2 & 521.1 & 392.0 & 256.9 \\
\hline
\end{array}
\]

Number of coefficients assumed unequal zero

\[
\begin{array}{c|c|c|c|c}
\hline
B_{(B)} & 45.3 \pm 8.5 & 56.4 \pm 6.2 & 66.98 \pm 0.35 & 66.87 \pm 0.42 \\
B_{(t)} & 10.6 & 18.0 & 382.4 & 315.1 \\
A_{(B)} & 0.075 \pm 0.017 & 0.106 \pm 0.015 & 0.1511 \pm 0.0013 & 0.1504 \pm 0.0019 \\
A_{(t)} & 8.9 & 13.9 & 236.6 & 155.3 \\
B_{(K)} & 0.0190 \pm 0.0078 & 0.497 \pm 0.012 & 0.482 \pm 0.033 & 0.482 \pm 0.033 \\
B_{(K)} & 4.9 & 79.8 & 29.2 & 29.2 \\
B_{(C)} & 0.722 \pm 0.019 & 0.698 \pm 0.054 & 25.5 & 25.5 \\
B_{(C)} & 76.8 & -0.29 \pm 0.41 & 0.94 & 0.94 \\
F & 24.1 & 5897 & 0.9 & 0.9 \\
\hline
\end{array}
\]

Table 2. Results of multiple regression according to (26). F- and t-test for absorption measurements at \( \tilde{v} = 18 \cdot 10^5 \text{ m}^{-1}. \)
Table 3. Best estimators for the coefficients $A_{v1}$ and $A_{v2}$ at 298.15 K.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\psi$</th>
<th>$A_{v1}$</th>
<th>$A_{v2}$</th>
<th>$A_{v2}(\psi^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_v$</td>
<td>1 mol m$^{-3}$</td>
<td>0.15098 ± 0.00032</td>
<td>7.335 ± 0.072</td>
<td></td>
</tr>
<tr>
<td>$w_v$</td>
<td>1</td>
<td>1476.3 ± 3.2</td>
<td>71290 ± 690</td>
<td></td>
</tr>
<tr>
<td>$x_v$</td>
<td>1</td>
<td>1559.6 ± 3.3</td>
<td>79420 ± 770</td>
<td></td>
</tr>
<tr>
<td>$r_v$</td>
<td>1</td>
<td>1559.6 ± 3.3</td>
<td>80980 ± 770</td>
<td></td>
</tr>
</tbody>
</table>

The value of the quantity $A_{v1}$ is according to (20) directly related to the value of $K_{v1}^*$ of the equilibrium constant of the formation of the 1:1 complex HMB-TCNE. For the interpretation of the quantity $A_{v2}$ according to (21) the assumption $K_{v20}^* = 0$ has to be introduced (compare Section 2.3). The value of $A_{v2}$ is then caused by the equilibrium constant $K_{v21}^*$ of the formation of the 2:1 complex (HMB)$_2$-TCNE and/or by the coefficient $\eta_{v11.10}$, which describes according to (7) the first-order activity effect on the 1:1 complex formation. Assuming $\eta_{v11.10} = 0$, it becomes

$$K_{v21}^* = A_{v2} \chi_3 \chi_2^{-1}(\psi^2)^2,$$

assuming $K_{v21}^* = 0$ it will be $\eta_{v11.10} = A_{v2}/A_{v1}$, the values are listed in Table 5.

If the assumption $\eta_{v11.10} = 0$ for $\alpha_1, \alpha_2 = 0, 1, 2, \ldots$, which is equivalent to $F_{v11} = 0$, is met for one concentration variable $\psi_j^{(n)}$ it usually will not be true for another concentration variable $\psi_j^{(n)}$ as has been discussed at (IV.44). The relations between the coefficients $\eta_{v11.10}$ are

$$\eta_{v11.10} = \frac{M_2 V_{v1}^*}{M_1} \eta_{v11.10} + M_1 V_{v0}^* - M_2 V_{v0}^* = V_{v0}^* \eta_{v11.10} + V_{v0}^* - V_{v0}^* = V_{v0}^* \eta_{v11.10} + V_{v0}^*.$$

The values of $\eta_{v11.10}$, which are different from zero for all but at least one concentration variable $\psi_j^{(n)}$, cause contributions to the estimators of $A_{v1}$ and $A_{v2}$ as listed in Table 3. Hence the values of $K_{v1}^*$ and $K_{v21}$, for example, obtained from $A_{v1}$ and $A_{v2}$, show some deviations from the values obtained from $K_{v1}^*$ and $K_{v21}^* (\psi = c)$ using (IV.43) as may be seen from the data in Table 5, the deviations of $K_{v21}^*$ are even larger if the contributions due to the term $K_{v11}^*$ $\eta_{v11.10}$ are taken into account (sixth row of Table 5). The problem of the choice of the most appropriate concentration variable for the evaluation of data was investigated by many authors.

Table 4. Best estimators for the coefficients $B_{xK1}$ and $B_{xK2}$ and molar absorption coefficients of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K.

<table>
<thead>
<tr>
<th>$\psi$</th>
<th>$10^5$ m$^{-1}$ B$_{xK1}$/10$^{-3}$ m$^{-1}$·mol$^{-2}$</th>
<th>B$_{xK2}$/10$^{-5}$ m$^2$·mol$^{-3}$</th>
<th>$x_{v1}^0/m^2$</th>
<th>$x_{v2}^0/m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>51618 ± 42</td>
<td>39486 ± 25</td>
<td>341.9 ± 0.8</td>
<td>538 ± 5</td>
</tr>
<tr>
<td>18</td>
<td>66827 ± 48</td>
<td>50367 ± 28</td>
<td>422.8 ± 1.0</td>
<td>687 ± 7</td>
</tr>
<tr>
<td>19</td>
<td>69648 ± 38</td>
<td>49867 ± 23</td>
<td>461.3 ± 1.0</td>
<td>677 ± 7</td>
</tr>
<tr>
<td>20</td>
<td>61180 ± 40</td>
<td>41588 ± 12</td>
<td>405.2 ± 0.9</td>
<td>567 ± 6</td>
</tr>
<tr>
<td>21</td>
<td>45089 ± 32</td>
<td>30866 ± 19</td>
<td>298.7 ± 0.7</td>
<td>422 ± 4</td>
</tr>
<tr>
<td>22</td>
<td>28558 ± 28</td>
<td>20474 ± 17</td>
<td>189.2 ± 0.5</td>
<td>279 ± 3</td>
</tr>
</tbody>
</table>
[20, 24, 29, 30, 49—51]; the best choice would be 
that one, where the terms $\eta_{\psi_{i} \alpha_{i} \omega_{i}} \psi_{\omega_{0}} \psi_{\omega_{3}}$ in (7) give 
the smallest contribution to $F_{\psi_{i} \alpha_{i}}$. An analysis of 
variance (F-test and t-test) of the data according 
to (26) including the term $A_{i} K_{M}^{*} (\psi_{\omega_{0}})^{2}$ on the right-
hand side, does not lead to a statistically significant
assertion even if the term seems to contribute the 
least for $\psi_{\omega_{0}} = c_{\omega_{0}}$; this gives some preference to 
this concentration variable and will therefore usually 
be chosen for the further evaluations in this study. The 
imperfect knowledge of the best choice of the con-
centration variable causes errors of the equilibrium 
constants $K_{c11}^{*}$ and $K_{c21}^{*}$ of the order of the difference 
of the different values listed in Table 5 (first 
column and fourth to sixth row), i.e. 0.3% for $K_{c21}^{*}$ 
and 4% for $K_{c21}^{*}$, and hence larger than the errors 
listed in Table 5, which are, as usual in this study, 
95% confidence limits based on the Student’s t-
distribution ($\pm t_{1-2} s$, where $s$ is the standard deviation 
of the mean and $z = 0.025$).

For optical absorption measurements, where the 
density $D_{\phi}$ was identified with the absorption coeffi-
cient $a$, the MMQ’s $\varphi_i$ occurring in (14) and (15) 
must, according to Sect. 9.4 of paper I, be identified 
with the molar absorption coefficient $x_{J}^{*}$ of sub-
stance $A_{J}$. Since in the considered wavenumber 
interval it is $x_{1}^{*} = x_{2}^{*} = x_{3}^{*} = 0$, one can assume 
$\lambda_{c11.0} x_{23} = 0$, for $J = 1, 2, 3$; $x_{2} = 0, 1, 2, \ldots$; $x_{3} = 
0, 1, 2, \ldots$, as has been discussed in paper I. Hence 
from (23) and (24), it follows that the molar ab-
sorption coefficients of the 1:1 complex are $x_{11}^{*} = 
B_{\kappa_{1}} / A_{c1}$; the values are listed in Table 4 and drawn 
in Figure 1. Assuming as above $K_{c20} = 0$ and $\eta_{c11.0} = 0$ it is 

$$B_{\kappa_{1}} = A_{2c} (x_{21}^{*} - 2 x_{2}^{*}) + A_{c1} \lambda_{c11.10}$$

$\lambda_{c11.10}$ describes according to Eq. (14) the solvent 
dependence of the molar absorption coefficient $x_{11}$ 
of the 1:1 complex in first-order relating to $c_{\omega_{0}}$. 
Assuming $\lambda_{c11.10} = 0$, then the molar absorption co.
efficients $x_{21}^{*} = B_{\kappa_{2}} / A_{c2}$ of the 2:1 complex can be 
calculated. The values are listed in Table 4 and drawn 
in Figure 1. Assuming $K_{c20} = 0$ and $K_{c21}^{*} = 0$, then 

$$B_{\kappa_{2}} = A_{c1} (x_{21}^{*} \eta_{c11.10} + \lambda_{c11.10})$$

and the values of $\lambda_{c11.10}$ can be calculated, as they 
are represented in Figure 1.

According to the above results the dependence of the 
optical absorption coefficients of solutions of 
HMB and TCNE in CCl$_4$, on their concentrations, 
can consistently be explained by two different 
models. According to model I, there exist two com-
plexes HMB-TCNE and (HMB)$_2$-TCNE, each one 
having an absorption band in the same wavenumber 
interval as shown in Figure 1. According to model II 
there exists just one complex, namely HMB-TCNE, 
and the further concentration dependences of the 
optical absorptions are caused by (1) the coefficient 
$\eta_{c11.10}$, which represents the activity effects on the 
quantity $K_{c11}$ of the complex formation, and (2) the 
coefficient $\lambda_{c11.10}$, which represents the solvent 
dependence of the molar absorption coefficient $x_{11}$ of

### Table 5. Equilibrium constants $K_{\psi_{11}}^{*}$ and $K_{\psi_{21}}^{*}$ for the formation of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K.

<table>
<thead>
<tr>
<th>$\psi_{J}$</th>
<th>$\psi_{\omega}^{G}$</th>
<th>Remark</th>
<th>$c_{J}$ (1 mol m$^{-3}$)</th>
<th>$\psi_{J}$</th>
<th>$x_{J}$</th>
<th>$r_{J}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\psi_{11}}^{*}$</td>
<td>1</td>
<td>0.15098 ± 0.00032</td>
<td>3346.6 ± 6.8</td>
<td>1557.6 ± 3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{\psi_{21}}^{*}$</td>
<td>2</td>
<td>(7.335 ± 0.072) $\times 10^{-4}$</td>
<td>251900 ± 2400</td>
<td>79420 ± 770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta_{c11.10} \psi_{\omega}^{G}$</td>
<td>3</td>
<td>(4.858 ± 0.049) $\times 10^{-3}$</td>
<td>48.29 ± 0.48</td>
<td>50.99 ± 0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{\psi_{21}}^{*}$</td>
<td>4</td>
<td>0.15119 ± 0.00032</td>
<td>0.15121 ± 0.00032</td>
<td>0.15140 ± 0.00032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{\psi_{21}}^{*}$</td>
<td>5</td>
<td>7.477 ± 0.071</td>
<td>7.485 ± 0.073</td>
<td>7.632 ± 0.073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta_{\psi_{11.10}} \psi_{\omega}^{G}$</td>
<td>6</td>
<td>7.592 ± 0.072</td>
<td>7.608 ± 0.073</td>
<td>7.902 ± 0.073</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remarks: 1. From the values $A_{\psi_{11}}$, Table 3.
2. From the values $A_{\psi_{21}}$, Table 3, assuming $K_{\psi_{20}}^{*} = 0$ and $\eta_{\psi_{11.10}} = 0$.
3. From the values $A_{\psi_{11}}, A_{\psi_{21}}$, Table 3, assuming $K_{\psi_{20}}^{*} = 0$ and $K_{\psi_{21}}^{*} = 0$.
4. Calculated from $K_{\psi_{21}}^{*}$ or $K_{\psi_{21}}^{*}$, respectively, using (IV. 43) (assuming $\eta_{\psi_{11.10}} = 0$).
5. Calculated from $K_{\psi_{21}}^{*}$ using (21) and (IV. 43) assuming $\eta_{c11.10} = 0$ but values of $\eta_{\psi_{11.10}} \psi_c$ as calcul-
   rated from (28) and listed in the last row of Table 5.
6. Calculated using (28) assuming $\eta_{c11.10} = 0$. 


the complex. A decision between these models is only possible if other data are known; for example, if the coefficients $\eta_{c1.10}$ and $\lambda_{c1.11.10}$ can be determined independently.

According to (7), (4) and (I.134) it is

$$\eta_{c1.10} = \left( \frac{\partial F_{c11}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} = \left( \frac{\partial \ln (f_{e2} f_e f_{c11})}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta}, \tag{29}$$

where $f_{eI}$ is the activity coefficient of the substance $A_I$ defined by (I.132) and (I.133). From (I.136) follows

$$\left( \frac{\partial \ln f_{eI}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} = \frac{1}{RT} \left[ \left( \frac{\partial g_{mI}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} + V^* \left( \frac{\partial g_{mI}}{\partial n_{I'}} \right)_{n_{I'}, \theta} \right]$$

$$+ n_{c01} \left( \frac{\partial}{\partial C_{c02}} \left( \frac{\partial g_{mI}}{\partial n_{I'}} \right)_{n_{I'}, \theta} \right)_{n_{c1.10}, c_{02}, \theta} + v_I^* \frac{\partial}{\partial V_{01}} \left( \frac{\partial g_{mI}}{\partial V_{01}} \right)_{n_{c1.10}, c_{02}, \theta}, \tag{30}$$

where $g_{mI}$ is a contribution to the model molar Gibbs energy $g_{I}$ of the substance $A_I$ in the solution defined by (I.120), $R$ is the gas constant, $V^*_I$ is the molar volume of the pure solvent (CCl4), $v_I$ is the model molar volume of the substance $A_I$ and $\lambda_{c1.10}$ is one coefficient of the power-series (14) for $G_{I} = v_I$. Application of (I.17) and introducing (30) into (29) leads to

$$\eta_{c1.10} = \frac{1}{RT} \left[ \left( \frac{\partial g_{mI}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} + \left( \frac{\partial g_{mII}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} - \left( \frac{\partial g_{mII}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} \right]$$

$$+ (v_{11}^* - v_{22}^* - v_{33}^*) (1 - v_{11}^* V_{01}) + \left( 1/V_{01} \right) \left( \lambda_{c1.11} - \lambda_{c1.20} - \lambda_{c1.30} \right). \tag{31}$$

The quantities $g_{mI}$ are dependent on the composition of the solution, a main contribution being caused by the electrostatic interactions of a solute molecule with the surrounding molecules of the solution [52]. Neglecting the other composition dependent contributions to $g_{mI}$, which is at least a rough approximation for the considered dilute solutions, $g_{mI}$ can be represented by [52]

$$g_{mI} = g_{mI}^* - \frac{N_A}{2} \mu_{gI} \left[ \left( 1 - f_I (er) \alpha_{gI} \right) ^{-1} f_I (er) \right.$$

$$\left. - \left( 1 - f_I (er^*) \alpha_{gI} \right) ^{-1} f_I (er^*) \right] \mu_{gI},$$

where $N_A$ is the Avogadro constant, $\mu_{gI}$ and $\alpha_{gI}$ are the electric dipole moment and the polarizability of a molecule $A_I$ (in the electronic ground state) and $er$ is the relative permittivity of the solution with the value $er^*$ of the pure solvent. The tensor function $f_I (er)$ is defined by (II.35). According to (32) $g_{mI}$ can be considered as a function of $er$, and hence

$$\left( \frac{\partial g_{mI}}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta} = \left( \frac{\partial g_{mI}}{\partial er} \right)_{\theta} \left( \frac{\partial er}{\partial C_{c02}} \right)_{n_{c1.10}, c_{02}, \theta}, \tag{33}$$

where because of (32)

$$\frac{1}{RT} \left( \frac{\partial g_{mI}}{\partial er} \right)_{\theta} = - \frac{1}{2kT} \mu_{gI} \left( 1 - f_I (er) \alpha_{gI} \right) ^{-2} \left( \frac{\partial f_I}{\partial er} \right)_{\theta}, \tag{34}$$

and because of Eq. (II.35)

$$\left( \frac{\partial f_I}{\partial er} \right)_{\theta} = \frac{f_I}{(er - 1)(er - \kappa er (er - 1))}, \tag{35}$$

Fig. 1. Molar absorption coefficients $x_{c1}^*$ and $x_{d1}^*$ of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl4 at 298.15 K and coefficients $\lambda_{c111.10}$, estimated from the data, and ($\lambda_{c111.10}$)calc, calculated according to (37). For ($\lambda_{c111.10}$)calc the scale factor on the right-hand side of the figure has to be multiplied by $10^{-3}$.
In Sect. 4.2 the limits $v_1^*$, $v_3^*$ and $v_{11}^*$ of the model molar volumes are estimated and it is shown that one has to assume $\lambda_{c11.10} = 0$, $I = 2$, 3, 11. In Section 4.3 the quantities $\mu_{sl}$, $\alpha_{sl}$, $f_{IA}$ and $\alpha_{11}$ and the derivative $(\partial \alpha_{11}/\partial \omega_{02})_{m_{11},c_{02},\phi_i}$ are estimated. With these data, listed in Tables 12 and 10, Eqs. (31) to (35) lead to

$$\eta_{c11.10}^{\text{calc}} = 1.28 \cdot 10^{-5} \text{ mol}^{-1} \text{ m}^3.$$

The model molar absorption coefficient $\kappa_{11}$ of HMB-TCNE depends on the relative permittivity $\varepsilon_r$ and the square $n^2$ of the refractive index of the solution, which may be represented by an equation similar to (33) of a previous paper [53]

$$\kappa_I(\varepsilon_r, n^2) \bar{\nu} = \frac{1}{2} S g_I(\bar{\nu}(\varepsilon_r, n^2)) - A \bar{\nu}_I(\varepsilon_r, n^2; \varepsilon_r^*, n^2^*) - \alpha_{11}[E_{RMI}(\varepsilon_r, n^2) - E_{RMI}(\varepsilon_r^*, n^2^*)]^2,$$

where $S = 2\pi^2 N_A \log e/h c_0 = 2.93512 \cdot 10^{60} \text{ C}^{-2} \text{ mol}^{-1}$,

$$s_I(\bar{\nu}(\varepsilon_r, n^2))$$

is the bandshape function of the considered electronic absorption band, $A\bar{\nu}_I$ is the shift of a transition between definite states if the relative permittivity and the square of the refractive index of the solvent is changed from $\varepsilon_r^*$ to $\varepsilon_r$ and from $n^2^*$ to $n^2$, $\mu_{11}(\varepsilon_r, n^2)$ is the electric transition dipole moment and $\alpha_{11}$ the transition polarization of the electronic band and $E_{RMI}(\varepsilon_r, n^2)$ the effective electric field in a solution with given values of $\varepsilon_r$ and $n^2$. Corresponding to (14) and (36) the coefficient $\lambda_{c11.10}(\bar{\nu})$ can be represented as

$$\lambda_{c11.10}(\bar{\nu}) = \left(\frac{\partial \kappa_{11}(\bar{\nu})}{\partial \omega_{02}}\right)_{m_{11},c_{02},\phi_i} = \left(\frac{\partial \kappa_{11}(\bar{\nu})}{\partial \varepsilon_r}\right)_{\phi_i} \left(\frac{\partial \kappa_{11}(\bar{\nu})}{\partial \omega_{02}/m_{11},c_{02},\phi_i} + \left(\frac{\partial \kappa_{11}(\bar{\nu})}{\partial n^2}\right)_{\phi_i} \left(\frac{\partial \kappa_{11}(\bar{\nu})}{\partial \omega_{02}/m_{11},c_{02},\phi_i}\right).$$

Neglecting the change of polarizability during the absorption process, i.e. assuming $\alpha_{sl} = \alpha_{gl}$, from (23) [54] follows for the shift

$$h c A \bar{\nu}_I(\varepsilon_r, n^2; 1,1) = h c (\bar{\nu} - \bar{\nu}_0) = \left(-\frac{1}{2} (\mu_{sl} - \mu_{gl}) (1 - f_I \alpha_{sl})^{-1} f_I (\mu_{sl} - \mu_{gl}) - (\mu_{sl} - \mu_{gl}) (1 - f_I \alpha_{sl})^{-1} f_I \mu_{sl}\right),$$

where $f_I(\varepsilon_I)$ is defined by (II.35) and (II.36) and $f_I = f_I(n^2)$. $\mu_{sl}$ is the electric dipole moment of the molecule $\Lambda_I$ in the considered excited electronic state. According to (22) [55] it is again with $\alpha_{sl} = \alpha_{gl}$

$$E_{RMI} = (1 - f_I \alpha_{sl})^{-1} f_I \mu_{sl} + \frac{1}{2} (1 - f_I \alpha_{sl})^{-1} f_I (\mu_{sl} - \mu_{gl}).$$

From the results reported in Sect. 4.4 it follows that the EDA complex HMB-TCNE owns, at least in a very good approximation, the symmetry of the point group $C_{2v}$ and that the considered electron donor-acceptor transition is of the $\Lambda_1 \rightarrow \Lambda_1$ type, i.e. the dipole moments $\mu_{sl}$ and $\mu_{al}$ and the transition dipole moment $\mu_{slal}$ are parallel to the $z$ axis of the complex (perpendicular to the plane of the HMB molecule). For such a transition it follows according to (7) and (9) of a previous paper [56] from (36)

$$h c \left(\frac{\partial \Delta \bar{\nu}_I}{\partial \varepsilon_r}\right)_{\phi_i} = \left(-\frac{1}{2} (\mu_{sl} - \mu_{gl}) (1 - f_I \alpha_{sl})^{-1} \mu_{sl} - \mu_{gl}, (41)$$

and a similar equation for $(\partial \kappa_{gl}/\partial n^2)_{\phi_i}$, where $\varepsilon_I$ has to be replaced by $n^2$ in (40). From (40) follows

$$h c \left(\frac{\partial \Delta \bar{\nu}_I}{\partial n^2}\right)_{\phi_i} = \left(-\frac{1}{2} (\mu_{al} - \mu_{gl}) (1 - f_I \alpha_{al})^{-2} \left(\frac{\partial \bar{\nu}_I}{\partial \varepsilon_r}\right)_{\phi_i} (\mu_{al} - \mu_{gl}), (42)$$

and from Eq. (39)

$$\left(\frac{\partial E_{RMI}}{\partial \varepsilon_r}\right)_{\phi_i} = (1 - f_I \alpha_{gl})^{-2} \left(\frac{\partial f_I}{\partial \varepsilon_r}\right)_{\phi_i} \mu_{gl}, (43)$$

$$\left(\frac{\partial E_{RMI}}{\partial n^2}\right)_{\phi_i} = \frac{1}{2} (1 - f_I \alpha_{gl})^{-2} \left(\frac{\partial f_I}{\partial n^2}\right)_{\phi_i} (\mu_{al} - \mu_{gl}). (44)$$

The derivative $(\partial \kappa_{gl}/\partial \varepsilon_r)_{\phi_i}$ is given by (35); for the derivative $(\partial \delta f_I/\partial n^2)_{\phi_i}$ a similar equation holds true, where $\varepsilon_I$ has to be replaced by $n^2$. 
In this section, the magnitude $|\mu_{ea11}|$ of the transition dipole moment will be estimated, and in Sect. 4.4, the values of $\mu_{a12}$ and $(x_{ea1})_{xz}$. The derivatives $(\partial \ln (x_{11} \tilde{r})/\partial \tilde{r})_{T, z}^{\tilde{r}}$, which are also needed for the evaluation of electro-optical absorption measurements in Sect. 4.4, can be obtained from the estimated values of $x_{11}^{*}$ as shown in Figure 1. With these data, listed in Tables 12 and 14, Eqs. (37) and (41) to (44) lead to the values $(\lambda_{x11.10})_{calc}$ as represented in Figure 1.

The value $(\eta_{c11.10})_{calc}$ calculated from (31) is approximately 0.3% of the value of $\eta_{c11.10}$ estimated from the data assuming model II (compare Table 5), the values of $(\lambda_{x11.10})_{calc}$ calculated from (37) are less than 0.1% of the values of $\lambda_{x11.10}$ estimated assuming model II. Hence comparison of calculated and estimated coefficients $\eta_{c11.10}$ and $\lambda_{x11.10}$ disclose that only model I agrees with the observed data. For estimations based on model I the coefficients are negligibly small compared to $K_{e11}^{*}$ and $x_{e11}^{*}$, respectively, and therefore the values of these quantities as reported in Table 5 and Table 4, may be considered as true values, taking the effects due to activity coefficients and the solvent dependence less than 0.1% of the values of $\lambda_{x11.10}$.

The numbers of optical absorption measurements at 283.15 K, 293.15 K and 298.15 K have been too small to allow a similar evaluation of data for the estimation of the coefficients of (19) with sufficiently small errors. Hence the data were evaluated assuming model I and temperature independent values of $x_{11}^{*}$ and $x_{e11}^{*}$ and negligible contributions due to $\lambda_{x11.10}$ and $\eta_{c11.10}$. The data confirm the assumptions, i.e. the quantities $B_{e11}/A_{e1}$ and $B_{e11}/A_{e2}$ depend on $\tilde{r}$ but depend neither on the composition of the solutions nor on their temperature in the investigated temperature interval. The results are listed in Table 6. From the values of $K_{e11}^{*}$ and $K_{e21}^{*}$ the model standard reaction enthalpies $\Delta R_{g}^{*}$, the model standard reaction entropies $\Delta S_{g}^{*}$ and the model standard reaction Gibbs energies $\Delta G_{g}^{*}$ can be estimated using (IV.35), (IV.39), and (IV.41). The values are listed in Table 7.

The values of the maximal absorption coefficient $(\bar{r}_{11})_{max} = 466 \text{ m}^2 \text{ mol}^{-1}$ at 
$$(\bar{r}_{11})_{max} = 1.87 \cdot 10^6 \text{ m}^{-1} \text{ and of }$$ $\Delta_{11}h_{g}^{*} = -32.9 \cdot 10^3 \text{ J} \text{ mol}^{-1}$ obtained in our studies for the complex HMB-TCNE are in excellent agreement with the data obtained by Briegleb, Czekalla and Reuss [16].

$\lambda_{max} = 478 \text{ m}^2 \text{ mol}^{-1}$, $\tilde{r}_{max} = 1.88 \cdot 10^6 \text{ m}^{-1}$ and $\Delta_{11}h_{g}^{*} = -32.4 \cdot 10^3 \text{ J} \text{ mol}^{-1}$ in spite of the fact that they considered only the formation of the 1:1 complex HMB-TCNE. The value of $K_{e11}^{*} = 0.148$ at 293 K is somewhat smaller than our value. One has to assume that they have restricted their investigation to small values of $c_{02}$, where the 2:1 complex formation gives only a negligible contribution to the observed optical absorption of the solution. The data reported by Ewall and Sonnessa [23], $K_{e11}^{*} = 0.123$ (at 298 K) and $x_{max} = 514 \text{ m}^2 \text{ mol}^{-1}$ and by Liao and Chan [58] $K_{e11}^{*} = 0.099$ (at 298 K) and $\Lambda_{11}h_{g}^{*} = -27 \cdot 10^3 \text{ J} \text{ mol}^{-1}$, where only the 1:1 complex formation was taken into account, show also some deviations from our results. The values of $K_{e11}^{*} = 0.180$ and $K_{e21}^{*} = 1.10 \cdot 10^{-3}$ at 293 K obtained by Foster and Kulevsky [17] are 5% and 23% lower than our values. Further data reported

Table 6. Equilibrium constants for the formation of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CC1$_4$ ($c^0 = 1 \text{ mol m}^{-3}$).

<table>
<thead>
<tr>
<th>$T$</th>
<th>$K_{e11}^{*}/10^{-4}$</th>
<th>$K_{e21}^{*}/10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.15</td>
<td>3032 ± 85</td>
<td>4300 ± 340</td>
</tr>
<tr>
<td>293.15</td>
<td>1901 ± 46</td>
<td>1424 ± 62</td>
</tr>
<tr>
<td>298.15</td>
<td>1510 ± 3</td>
<td>734 ± 7</td>
</tr>
<tr>
<td>303.15</td>
<td>1188 ± 22</td>
<td>506 ± 19</td>
</tr>
</tbody>
</table>

Table 7. Model standard reaction quantities for the formation of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CC1$_4$ at 298.15 K ($c^0 = 1 \text{ mol m}^{-3}$).

<table>
<thead>
<tr>
<th>$R$</th>
<th>HMB-TCNE (1)</th>
<th>(HMB)$_2$-TCNE (21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta R_{g}^{*}/\text{J mol}^{-1}$</td>
<td>4685.9 ± 0.5</td>
<td>17890 ± 25</td>
</tr>
<tr>
<td>$\Delta R_{g}^{*}/10^3 \text{ J mol}^{-1}$</td>
<td>-32.9 ± 1.9</td>
<td>-78 ± 16</td>
</tr>
<tr>
<td>$\Delta R_{g}^{*}/\text{J mol}^{-1} K^{-1}$</td>
<td>-126.0 ± 6.4</td>
<td>-322 ± 54</td>
</tr>
</tbody>
</table>
on the HMB-TCNE system [5, 12, 15, 23, 40, 41, 44, 45] have been measured in other solvents and therefore cannot be compared directly with our results. We just want to mention that the calorimetric determined value of the standard reaction enthalpy $\Delta_{11}^{\neq} = -31.27 \cdot 10^3 \text{J mol}^{-1}$ in CH$_2$Cl$_2$ obtained by Herndon, Feuer and Mitchell [9] agrees well with our value, also because they investigated only the interval $c_{02} = 20$ to 100 mol m$^{-3}$, where the formation of the 2:1 complex is rather small.

4.2. Density Measurements

The densities $\rho$ were measured of 23 sets of solutions in CCl$_4$ at 298.15 K with fixed values of the mass fraction $w_{03}^{+}$ of HMB, each set consisting of a few solutions with variable values of the mass fraction $w_{03}$ of TCNE ($c_{03}^{+} = 32$ to 510 mol m$^{-3}$, $c_{03} = 5$ to 28 mol m$^{-3}$). Analysis of the variance (F- and t-test) of the data has shown that in the investigated concentration intervals the inverse density $\rho^{-1}$ is linearly dependent on the mass fraction $w_{03}$. Hence (1) is simplified to

$$\frac{1}{\rho} = \frac{1}{\rho^*} + \left(\frac{V_{03}^+}{M_3} - \frac{1}{\rho^+}\right)w_{03}, \quad (45)$$

where $V_{03}^+$ is the limit of the partial molar volume for $w_{03} \rightarrow 0$ and $M_3$ is the molar mass of TCNE. From the data and (45) the values of $V_{03}^+$ and $\rho^+$ are determined.

In the investigated concentration interval $1/\rho^+$ is linearly dependent on $w_{02}^+$ as has been shown again by analysis of variance. Hence (II.17) is simplified to

$$\frac{1}{\rho^+} = \frac{1}{\rho^{*+}} + \left(\frac{V_{02}^+}{M_2} - \frac{1}{\rho^{*+}}\right)w_{02}^+, \quad (46)$$

where $V_{02}^+$ is the limit of the partial molar volume $V_{02}$ of HMB for $w_{02}^+ \rightarrow 0$ (and $w_{03} \rightarrow 0$) and $\rho^+$ is the density of the pure solvent. The values obtained $\rho^* = (1584.718 \pm 0.010)$ kg m$^{-3}$ and

$$V_{02}^+ = (175.31 \pm 0.07) \cdot 10^{-6} \text{m}^3\text{mol}^{-1}$$

agree excellently with those of Le Fèvre [59].

The values of $V_{03}^+$ are represented in Figure 2. They can be evaluated according to (19). Since there are not so many data as have been available from optical absorption measurements and since the dependence of $V_{03}$ on the concentration $c_{02}$ does not deviate so strongly from linear behaviour as was found for $K_{03}^+$, the values of $A_{c1}$ and $A_{c2}$ obtained in Sect. 4.1 are used for the estimation of the coefficients $B_{c0}, B_{c1}, B_{c2}, \ldots$. The results of F- and t-test as listed in Table 8, show that the first three and only the first three coefficients are significantly different from zero.

For the further evaluation according to (22) to (24) some approximations have to be introduced. Since we do not know a model which describes the dependence of the model molar values $v_1, v_2$ and $v_3$ on the concentrations $c_{02}$ and $c_{03}$ of the solutions, the coefficients $\lambda_{02c_1a_{02a_0}}, J = 1, 2, 3$, have to be neglected. Assuming model I as introduced in Section 4.1 — the formation of the 1:1 and the 2:1 complex and $\eta_{c11.10} = 0$, $\lambda_{c11.10} = 0$ — the equations are simplified to

$$B_{v0} = V_{03}^*, \quad B_{c1} = A_{c1}(v_{11}^* - v_{22}^*), \quad B_{c2} = A_{c2}(v_{22}^* - 2v_{22}^*),$$

Table 8. Results of multiple regression according to (19), F- and t-test for density measurements of solutions of HMB and TCNE in CCl$_4$ at 298.15 K.

<table>
<thead>
<tr>
<th>Number of coefficients assumed unequal zero</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{0}/10^{-5}$ m$^3$ mol$^{-1}$</td>
<td>-46.5</td>
<td>$11.33 \pm 0.32$</td>
<td>11.01</td>
</tr>
<tr>
<td>$t(B_{0})$</td>
<td>6.4</td>
<td>71.8</td>
<td>44.8</td>
</tr>
<tr>
<td>$B^{1-7}_{c1}$ m$^6$ mol$^{-2}$</td>
<td>305.3</td>
<td>156.03 $\pm$ 0.71</td>
<td>157.08</td>
</tr>
<tr>
<td>$t(B^{1-7}_{c1})$</td>
<td>26.0</td>
<td>442.6</td>
<td>216.6</td>
</tr>
<tr>
<td>$B^{10^{-9}}_{c2}$ m$^9$ mol$^{-3}$</td>
<td>$-63.41 \pm 0.27$</td>
<td>62.56</td>
<td></td>
</tr>
<tr>
<td>$t(B^{10^{-9}}_{c2})$</td>
<td>$-477.7$</td>
<td>118.1</td>
<td></td>
</tr>
<tr>
<td>$B^{10^{-11}}_{c3}$ m$^{12}$ mol$^{-4}$</td>
<td>$-230000$</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>$-477.7$</td>
<td>118.1</td>
<td>0.153</td>
</tr>
</tbody>
</table>

![Fig. 2. Values of the limit $V_{03}^+$ of the partial molar volumes of TCNE for solutions of HMB and TCNE in CCl$_4$ at 298.15 K. The curve is calculated according to (19) using the data in Tables 2 and 8.](image-url)
where \( v_{11}^* \) and \( v_{21}^* \) are the limits of the model molar volumes \( v_{11} \) and \( v_{21} \) of the complexes HMB-TCNE and (HMB)\(_2\)-TCNE for \( w_{03} \rightarrow 0 \) and \( w_{03} \rightarrow 0 \). With the above data the following values are estimated

\[
\begin{align*}
V_{01}^* &= (97.067 \pm 0.001) \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \\
V_{02}^* &= (175.31 \pm 0.07) \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \\
V_{03}^* &= (113.3 \pm 3.2) \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \\
v_{11}^* &= (278.65 \pm 0.52) \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \\
v_{21}^* &= (437.07 \pm 0.92) \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}.
\end{align*}
\]

Assuming model II — the formation of only the 1:1 complex and \( \eta_{11,10} = 0 \) — leads to a modification of the equation for \( B_{cv} \)

\[
B_{cv} = A_{c2} v_{2}^* + A_{c1} \cdot \left[(\varepsilon^2)^{-1} \eta_{11,10} (v_{11}^* - v_{2}^*) + \lambda_{cv,11,10}\right].
\]

From the data follows

\[
\lambda_{cv,11,10} = -8.76 \cdot 10^{-8} \text{ m}^6 \text{ mol}^{-2}.
\]

The results can be explained quite naturally with model I. There is a decrease of the molar volumes \( \Delta v_{11}^* = -9.96 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1} \) and \( \Delta v_{21}^* = -26.85 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1} \) during the formation of the EDA-complexes HMB-TCNE and (HMB)\(_2\)-TCNE (3.6 and 6.1 %, respectively), caused by the shortening of the distances between the components of the complexes compared to the average distances of neighboring molecules in the solution. According to model II there would be a rather large dependence of the molar volume \( v_{11} \) of the complex HMB-TCNE on the concentration of HMB as described by the value of \( \lambda_{cv,11,10} \), namely a decrease of approximately 15% in the investigated concentration interval (\( c_{02} = 0 \) to 500 mol \( \cdot \) m\(^{-3} \)). Such a behavior of \( v_{11} \) is very improbable. Therefore the data obtained from density measurements also strongly support model I, i.e. the formation of both complexes HMB-TCNE and (HMB)\(_2\)-TCNE.

### 4.3. Permittivity and Refractometer Measurements

The relative permittivities \( \varepsilon_r \) and the refractive indices \( n \) at the wavenumber \( \tilde{v} = 9.259 \cdot 10^{5} \text{ m}^{-1} \) were measured of 20 sets of solutions in CCL\(_4\) at 298.15 K with fixed values of the mass fraction \( w_{02}^* \) of HMB; each set consisted of a few solutions with variable values of the mass fraction \( w_{03} \) of TCNE (\( c_{02}^* = 32 \) to 570 mol \( \cdot \) m\(^{-3} \), \( c_{03} = 0 \) to 41 mol \( \cdot \) m\(^{-3} \)).

Analysis of variance (F- and t-test) of the data has shown that in the investigated concentration intervals the specific electric susceptibility \( \varepsilon_r - 1 \) is linearly dependent on the mass fraction \( w_{03} \). Hence (1) is simplified to

\[
P_{nZ} = \varepsilon_r - 1 = \frac{\varepsilon_r^+ - 1}{\varepsilon_r^+} - \frac{Z_0^+}{M_3} \left( \frac{\varepsilon_r^+ - 1}{\varepsilon_r^+} \right) w_{03}, \quad (47)
\]

where \( \varepsilon_r^+ \) and \( Z_0^+ \) are the limits of the relative permittivity \( \varepsilon_r \) and of the partial molar electric susceptibility \( Z_0 \) of TCNE for \( w_{03} \rightarrow 0 \), respectively. Linear regression according to (47) leads to values for \( (\varepsilon_r^+ - 1)/\varepsilon_r^+ \) and \( Z_0^+ (w_{02}^*) \).

In the investigated concentration interval \( (\varepsilon_r^+ - 1)/\varepsilon_r^+ \) is linearly dependent on \( w_{02}^* \) as has been shown again by analysis of variance. Hence (II.6) is simplified to

\[
\varepsilon_r^+ - 1 = \frac{\varepsilon_r^* - 1}{\varepsilon_r^*} + \frac{Z_0^*}{M_3} - \frac{\varepsilon_r^* - 1}{\varepsilon_r^*} \left[ w_{02}^* \right], \quad (48)
\]

where \( \varepsilon_r^* \) and \( Z_0^* \) are the limits of the permittivity (permittivity of the pure solvent CCL\(_4\)) and of the partial molar electric susceptibility \( Z_0 \) of HMB for \( w_{02} \rightarrow 0 \), respectively. Linear regression according to (48) leads to values for \( (\varepsilon_r^* - 1)/\varepsilon_r^* \) and \( Z_0^* \).

Equations similar to (47) and (48) but with \( \varepsilon_r \) substituted by \( n^2 \) hold for \( P_{nZ} = (n^2 - 1)/n \). The evaluation of data leads to \( (n^2 - 1)/n \), \( Z_0^* \) and \( Z_0^+ (w_{02}^*) \).

With the value of \( n^2 \), Sect. 4.2, it results:

\[
\varepsilon_r = 2.22794 \pm 0.00006,
\]

\[
n^2 = 2.10431 \pm 0.00002.
\]

The errors given are only statistical ones. Due to the limited accuracy of the calibration of measuring devices the actual errors are to be expected larger. The values of \( Z_0^* \) and \( Z_0^+ \) obtained are listed in Table 12, the values of \( Z_0^* \) and \( Z_0^+ \) are represented in Figure 3. They can be evaluated according to (19) with a method similar to that one used for the evaluation of the partial molar volumes \( V_{03} \), Section 4.2. The results of the F- and t-test listed in Table 9, show that the first three and only the first three coefficients are significantly different from zero; multiple regression leads to the estimators for \( B_{Z0}, B_{Z1}, B_{Z2}, B_{Z3}, B_{Z1}, B_{Z2} \) and \( B_{Z3} \) as given in column \("3\) of Table 9.
The limit $Z^*_{02}$ of the partial molar electric susceptibility is related to the limit $\zeta^*_2$ of the model molar electric susceptibility of HMB according to (I.78) and (I.83) by

$$\zeta^*_2 = Z^*_{02} - \lambda_{c21.10} / V^*_1. \quad (49)$$

A similar equation holds for $\zeta^*_3$, where $Z^*_{03}$ is to be substituted by $Z^*_{02}$ and $\lambda_{c21.10}$ by $\lambda_{c31.10}$. Similarly

Table 9. Results of multiple regression according to (19), F- and t-test for refractometric and permittivity measurements of solutions of HMB and TCNE in CCl₄ at 298.15 K.

<table>
<thead>
<tr>
<th>Number of coefficients</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{20}$</td>
<td>$10^{-5}$ m$^3$ mol$^{-1}$</td>
<td>-215</td>
<td>16.5</td>
</tr>
<tr>
<td>$t(B_{20})$</td>
<td></td>
<td>5.6</td>
<td>7.0</td>
</tr>
<tr>
<td>$B_{21}$</td>
<td>$10^{-7}$ m$^3$ mol$^{-2}$</td>
<td>1677</td>
<td>1081</td>
</tr>
<tr>
<td>$t(B_{21})$</td>
<td></td>
<td>27.2</td>
<td>210.9</td>
</tr>
<tr>
<td>$B_{22}$</td>
<td>$10^{-9}$ m$^3$ mol$^{-3}$</td>
<td>224.8</td>
<td>3.4</td>
</tr>
<tr>
<td>$t(B_{22})$</td>
<td></td>
<td>134.6</td>
<td></td>
</tr>
<tr>
<td>$B_{30}$</td>
<td>$10^{-11}$ m$^2$ mol$^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t(B_{30})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{31}$</td>
<td>$10^{-5}$ m$^3$ mol$^{-1}$</td>
<td>-110</td>
<td>14.30</td>
</tr>
<tr>
<td>$t(B_{31})$</td>
<td></td>
<td>5.3</td>
<td>85.8</td>
</tr>
<tr>
<td>$B_{32}$</td>
<td>$10^{-7}$ m$^3$ mol$^{-2}$</td>
<td>550</td>
<td>231.17</td>
</tr>
<tr>
<td>$t(B_{32})$</td>
<td></td>
<td>16.7</td>
<td>639.7</td>
</tr>
<tr>
<td>$B_{33}$</td>
<td>$10^{-9}$ m$^3$ mol$^{-3}$</td>
<td>-120.64</td>
<td>0.24</td>
</tr>
<tr>
<td>$t(B_{33})$</td>
<td></td>
<td>-1022.9</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td></td>
<td>1.000000</td>
<td></td>
</tr>
</tbody>
</table>

for the further evaluation of the quantities $B_{20}, \ldots, B_{22}$ according to (22) to (24) some of the coefficients $\lambda_{c21.12}$ and $\lambda_{c31.21}$ are needed, which are defined by (14).

The further evaluation of the quantities $\zeta^*_2$ and $\zeta^*_3$, which may lead to the permanent electric dipole moment $\mu_{ef}$ or the static polarizability $\alpha_{ef}$ and the polarizability $\Delta_{ef}$ at the wavenumber $\bar{v}$ used for the investigation ($\bar{v} = 9.259 \times 10^3$ m$^{-1}$) of the molecule $\Lambda_{ef}$ in the electronic ground state, must be based on a suitable model, for which we choose the extended Onsager model in ellipsoidal approximation [37]. In accordance with this model the quantities $\zeta^*_2$ and $\zeta^*_3$, as represented by (II.41) and (II.51), are dependent on $\epsilon_r$ and $n^2$, respectively, at least at fixed values of the temperature $T$ and the pressure $p$. Hence

$$\lambda_{c21.10} = \left( \frac{\partial \zeta^*_1}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \right), \quad (50)$$

and

$$\lambda_{c31.20} = \frac{1}{2} \left( \frac{\partial \zeta^*_2}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} \right), \quad (51)$$

Similar equations hold true for $\lambda_{c21.01}$ and $\lambda_{c31.02}$, where the indices “2” and “3” have to be exchanged. The coefficients $\lambda_{c21.11}$ and $\lambda_{c31.21}$ can similarly be expressed. Representations for $\lambda_{c21.12}$ and $\lambda_{c31.21}$ result from similar equations, where $\epsilon_r$ is substituted by $n^2$.

The derivatives $(\partial \epsilon_r / \partial \epsilon_r)_{c2, \theta, \lambda}$, $(\partial \epsilon_r / \partial \epsilon_r)_{c3, \theta, \lambda}$, ... follow from (47), (48), (45) and (46), for example,

$$\left( \frac{\partial \epsilon_r}{\partial \epsilon_r} \right)_{c2, \theta, \lambda} = Z^*_{02} - (\epsilon_r - 1) V^*_1. \quad (52)$$

Similar equations hold for

$$(\partial n^2 / \partial \epsilon_r)_{c2, \theta, \lambda}, (\partial n^2 / \partial \epsilon_r)_{c3, \theta, \lambda}, \ldots$$

where $Z^*_{02}$ and $\epsilon_r$ have to be substituted by $Z^*_{03}$ and $n^2$. The data necessary for the estimation of the derivatives have been determined above and in Sect. 4.2, and the results are collected in Table 10.

The derivatives $(\partial \epsilon_r / \partial \epsilon_r)_{c2, \theta, \lambda}$, $(\partial o^2 / \partial \epsilon_r)_{c2, \theta, \lambda}$, ... follow from (II.41), and an example is given by (II.42). Similarly the derivatives $(\partial \zeta^*_2 / \partial \epsilon_r)_{c2, \theta, \lambda}$, ... follow from (II.51). For the derivatives with $I = 1$ the interaction radius $a_{w1}$ and the traces of the polariz-
Table 10. Derivatives of $y$ and $n^2$ with respect to $c_{02}$ and $\epsilon_{03}$ for solutions of HMB and TCNE in CCl$_4$ at 298.15 K.

<table>
<thead>
<tr>
<th>$y$</th>
<th>$\epsilon_r$</th>
<th>$n^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\partial y/\partial c_{02})^*_{ly} 10^{-6}$ m$^3$ mol$^{-1}$</td>
<td>32.17 ± 0.21</td>
<td>38.531 ± 0.068</td>
</tr>
<tr>
<td>$(\partial y/\partial \epsilon_{03})_{ly} 10^{-6}$ m$^3$ mol$^{-1}$</td>
<td>26 ± 48</td>
<td>17.9 ± 4.9</td>
</tr>
<tr>
<td>$(\partial^2 y/\partial c_{02} \partial \epsilon_{03})^*_{ly} 10^{-6}$ m$^3$ mol$^{-2}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(\partial^2 y/\partial c_{02} \partial \epsilon_{03})^*_{ly} 10^{-6}$ m$^3$ mol$^{-2}$</td>
<td>85.0 ± 7.3</td>
<td>31.9 ± 7.9</td>
</tr>
<tr>
<td>$(\partial n^2/\partial c_{02} \partial \epsilon_{03})^*_{ly} 10^{-6}$ m$^3$ mol$^{-2}$</td>
<td>−25.4 ± 2.2</td>
<td>−0.89 ± 0.23</td>
</tr>
</tbody>
</table>

The values of $\lambda_{c1} \cdot 10^3$ and $\lambda_{c2} \cdot 10^3$ obtained from (50) are listed in Table 11. With these data and $Z_{g2}$ or $Z_{g2}$ the values of $\xi_{g2}^*$ or $\xi_{g2}^*$ result according to (49); they are reported in Table 12. The details of the further evaluation of $\xi_{g2}^*$ and $\xi_{g2}^*$ leading to the polarizabilities $\alpha_{g2}$ and $\alpha_{g2}$ of HMB are given in a previous paper [37]. The data necessary and the results are also listed in Table 12.

In a similar way the quantities $B_{12}$ and $B_{12}^*$, Table 9, can be evaluated. According to (22) these data lead to $\xi_{s2}^*$ and $\xi_{s2}^*$ and as above to $\alpha_{g3}$ and $\alpha_{g3}$ of TCNE; the data necessary and the results are listed in Table 12.

With the values obtained for HMB and TCNE the derivatives $(\partial \xi_{s2}/\partial c_{02}), (\partial \xi_{s2}/\partial \epsilon_{03})$, ... can be calculated for $I = 2$ and 3 using (II.41) and (II.51). These quantities together with the derivatives $(\partial \epsilon_r/\partial c_{02}), ...$ as given in Table 10 allow the calculation of $\xi_{c1} \cdot 10^3$, $I = 2, 3$, (50) and similar equations; the results are listed in Table 11.

For the estimation of the interaction distances $(\alpha_{g11})_{ly} I = 11, \lambda = x, y, z$, a sandwich-type configuration (D-A) of the complex HMB-TCNE is assumed, where the planes of the molecules are parallel to each other ($xy$ plane) and the symmetry centers of the molecules are on the $z$ axis with a distance equal to $3.4 \cdot 10^{-10}$ m. The assumed configuration is confirmed by the results of electro-optical absorption measurements (Section 4.4). The electronic contribution to the polarizability of the complex was estimated according to (A11) and $\lambda_{c1} \cdot 10^3 + \lambda_{c2} \cdot 10^3$ assuming the described configuration. Similarly the static polarizability was estimated as

$$\alpha_{g11} = \alpha_{g2} + \alpha_{g3}$$

With these data the evaluation of $\xi_{g1}^*$ and $\xi_{g2}^*$ was done as described previously [37]. The data used and the obtained values of $(\mu_{g11})_{ly} I = 11, 3$, and $(\alpha_{g11})_{ly} I = 11, 3$ are listed in Table 12.

Assuming model I — the formation of the 1:1 and the 2:1 complex — from the quantities $B_{12}$ and $B_{12}^*$, Table 5, $A_{c1}$ and $A_{c2}$, the following model molar electric susceptibilities $\xi_{g1}^*$ and $\xi_{g2}^*$ of the complex (HMB)$_2$-TCNE can be obtained, if the values of the coefficients $\lambda_{c1} \cdot 10^3$ and $\lambda_{c2} \cdot 10^3$, $I = 1, 2, 3$, and 11, given in Table 11 are used. The coefficients with $J = 1, 2$ and 3 have been discussed above. The coefficients $\lambda_{c111} \cdot 10^3$ and $\lambda_{c211} \cdot 10^3$ can be calculated similarly, using (II.41) and (II.51) and the data obtained for the HMB-TCNE complex as listed in Table 12. The values of $\xi_{g1}^*$ and $\xi_{g2}^*$ are listed in Table 11.

Table 11. Estimated values of coefficients $\lambda_{c1} \cdot 10^3$ and $\lambda_{c2} \cdot 10^3$ needed for the evaluation of refractometric and permittivity measurements.
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Table 12. Determination of electric dipole moments and polarizabilities from measurements of solutions of HMB and TCNE in CCl₄ at 298.15 K.

<table>
<thead>
<tr>
<th>J</th>
<th>HMB</th>
<th>TCNE</th>
<th>HMB-TCNE</th>
<th>(HMB)₂-TCNE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mₗ/kg mol⁻¹</td>
<td>0.162274</td>
<td>0.128093</td>
<td>0.290367</td>
<td>0.452641</td>
</tr>
<tr>
<td>V₀/10⁻⁴</td>
<td>0.049995</td>
<td>0.049995</td>
<td>0.049995</td>
<td>0.049995</td>
</tr>
<tr>
<td>Z₀/10⁻⁶ m³ mol⁻¹</td>
<td>232.13 ± 0.06</td>
<td>143.0 ± 3.4</td>
<td>278.65 ± 0.52</td>
<td>437.07 ± 0.92</td>
</tr>
<tr>
<td>Z/10⁻⁶ m³ mol⁻¹</td>
<td>247.44 ± 0.21</td>
<td>165 ± 48</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10⁻⁴ CV- m²</td>
<td>15.05 ± 0.01</td>
<td>8.76 ± 0.22</td>
<td>39.24 ± 0.14</td>
<td>61.84 ± 0.14</td>
</tr>
<tr>
<td>10⁻³ CV- m²</td>
<td>29.31 ± 0.03</td>
<td>24.28 ± 0.01</td>
<td>14.79</td>
<td>41.84</td>
</tr>
<tr>
<td>10⁻² CV- m²</td>
<td>27.91 ± 0.01</td>
<td>27.91 ± 0.01</td>
<td>20.74 ± 0.37</td>
<td>39.07</td>
</tr>
<tr>
<td>10⁻¹ CV- m²</td>
<td>27.91 ± 0.01</td>
<td>27.91 ± 0.01</td>
<td>20.74 ± 0.37</td>
<td>39.07</td>
</tr>
<tr>
<td>10⁻² CV- m²</td>
<td>27.91 ± 0.01</td>
<td>27.91 ± 0.01</td>
<td>20.74 ± 0.37</td>
<td>39.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Remark: The values of (αₑJ)₀e, λ = x, y, z, J = 2, 3, 21, are estimated assuming µₑJ = 0 and (αₑJ)₀e/Tr(αₑJ)₀e

= (αₑJ)₀e/Tr(αₑJ)₀e.

Table 12. For the determination of γ₂x, γ₂y and γ₂z, a few of the coefficients \( \lambda_{c1x} \) and \( \lambda_{c2x} \) give only a negligible contribution \( \lambda_{c2x} = 0 \) and \( \lambda_{c2y} = 0 \) and the corresponding \( \lambda_{c2z} \). But, as we want to emphasize, this does not hold true for the coefficients generally. The coefficient \( \lambda_{c2z} \) contributes approximately 15% of the quantity \( B_{c2z} \) to \( \gamma_{c1} \); the coefficients \( \lambda_{c211} \) and \( \lambda_{c211} \) each contribute ten times as much to \( \gamma_{c2} \) as \( B_{c2z} \), but the sum of the contributions of both coefficients is very small for the considered (HMB)₂-TCNE complex.

For the estimation of the interaction distances \( (αₑJ)₀e, \) I = 21, \( \lambda = x, y, z, \) a sandwich-type configuration (D-A-D or D-D-A) of the complex (HMB)₂-TCNE is assumed, where the planes of the molecules are parallel to each other and the symmetry centers of the molecules are on the z axis with distances equal to 3.4 \( \times 10^{-10} \) m. The results of the dielectric and electro-optical absorption measurements (Section 4.4) confirm the configuration D-A-D. The polarizabilities of the complex were estimated according to \( (\alpha_{g2})_b = 2(\alpha_{g2})_oe + (\alpha_{g3})_oe \) and \( (\alpha_{g2})_a = 2(\alpha_{g3})_oe + (\alpha_{g3})_oe \) assuming the described configuration. With these data, the evaluation of \( \gamma_{c2} \) and \( \gamma_{c1} \) was done as above. The data used and the obtained values of \( (\mu_{g2})_oe, (\alpha_{g2})_oe \) and \( (\alpha_{g2})_oe \) are listed in Table 12.

Assuming model II — the formation of only the 1:1-complex — from the quantities \( B_{c2z} \) and \( B_{c2z} \), Table 9, the values of the coefficients

\[ \lambda_{c11} = -(1.83 ± 0.10) \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2} \]

and

\[ \lambda_{c211} = (2.8 ± 1.1) \cdot 10^{-8} \text{ m}^6 \text{ mol}^{-2} \]

can be estimated. Comparison with the values calculated using the extended Onsager model, Table 11,
shows that the first coefficient has the wrong sign and both coefficients have a wrong order of magnitude. These facts again falsify model II.

Dielectric and refractometric measurements of HMB and TCNE in CCl₄ at 293 K were also performed by Briegleb, Czekalla, and Reuss [16] in a concentration interval \( c_{o2} = 142 \) to \( 275 \) mol m\(^{-3}\), where the 2:1 complex formation is not negligible. Therefore the magnitude \( ||\mu_{g21}|| \) of the dipole moment estimated with the assumption of only 1:1 complex formation is expected to be erroneous \((4.50 \cdot 10^{-30} \text{ Cm})\). Their data have been evaluated again by Foster and Kulevsky [17], who estimated \( ||\mu_{g21}|| = (9.3 \pm 1.0) \cdot 10^{-30} \) and \( ||\mu_{g21}|| = (0 \pm 3.3) \cdot 10^{-30} \) Cm but with a method, with which it seems rather fortunate to obtain results, even of the right order of magnitude. The errors of the individual measurements (deviations) and the small interval of \( c_{o2} \) investigated make it very improbable that any method of evaluation could lead to reliable values of \( ||\mu_{g21}|| \) and \( ||\mu_{g21}|| \) as may be recognized from the data of Briegleb et al. in Figure 3. From measurements in CCl₄ at 298 K but only taking the formation of the 1:1 complex into account, Chan and Liao [60] obtained \( ||\mu_{g21}|| = 5.5 \cdot 10^{-30} \) Cm.

### 4.4. Electro-Optical Absorption Measurements

The quantity \( M \), defined by (1.166), characterizes the electro-optical absorption of isotropic solutions. These quantities were measured of eight solutions of HMB and TCNE in CCl₄ at 298.15 K at 20 wavenumbers in the interval \( \tilde{\nu} = 1.56 \) to 2.08 \( \cdot 10^4 \) m\(^{-1}\) \((c_{o3} = 8 \) to 370 mol m\(^{-3}\), \( c_{o3} = 0.04 \) to 0.17 mol m\(^{-3}\)). The data obtained have shown that in the investigated concentration intervals the specific electro-optical absorption \( P_{w3} = M/\omega \) is linearly dependent on \( \omega \) and in the investigated wavenumber interval the limit of \( P_{w3} \) for \( \omega \rightarrow 0 \) vanishes, i.e. \( P_{w3} = 0 \). Hence from (1) follows a simple relation for the determination of the limit \( Y_{03}^+ \) of the partial molar electro-optical absorption of TCNE in the solutions:

\[
Y_{03}^+ = \left[ \frac{1}{c_{o3}} \lim_{\varepsilon \rightarrow 0} \left( \frac{\partial a_E}{\partial E^2} \right) \right] = \left( \frac{M}{c_{o3}} \right)^+ = \frac{M}{c_{o3}}, (53)
\]

where \( a_E \) is the optical absorption coefficient of the solution in an applied electric field \( E_a \). At fixed values of \( T \) and \( p \) the PMQ \( Y_{03}^+ \) depends on \( c_{o2}^2 \), \( \tilde{\nu} \) and \( \chi \), where \( \chi \) is the angle between \( E_a \) and the polarization direction \( e \) of the incident plane polarized light wave with wavenumber \( \tilde{\nu} \). Some values of \( Y_{03}^+ \) are listed in Table 13 as examples. A set of quantities \( Y_{03}^+ \) with fixed values of \( \tilde{\nu} \) and \( \chi \) and variable values of \( c_{o3} \) satisfies (19), but in this case three coefficients \( K \) are not sufficient for an appropriate representation as will be shortly recognized.

Since under the considered conditions \( \chi_1 = \chi_2 = \chi_3 = 0 \) we may safely assume \( \nu_1 = \nu_2 = \nu_3 = 0 \), where \( \nu \) is the model molar electro-optical absorption of the molecule \( A_i \), compare III.2. Furthermore it is \( \lambda_{CQZ, CQ} = 0 \), for \( I = 1, 2 \) and 3. For model I the coefficients \( \eta_{CQ11.10} \) and \( \lambda_{CQ11.10} \) are vanishingly small, as has been shown in Sect. 4.1, and therefore \( \eta_{CQ11.10} \) and the field dependence of \( \eta_{CQ11.10} \) are negligible. With these presuppositions from (19) to (24) follows for the limit of \( (a_E/c_{o3}) \) in an applied electric field

\[
\left( \frac{\partial a_E}{\partial E^2} \right)^+ = \frac{x_{E21}^+ K_{E21}^+ c_{o3}^2 (c^2)^{-1} + x_{E21}^+ K_{E21}^+ (c_{o3}^2)^2 (c^2)^{-2} + 1 + K_{E21}^+ c_{o3}^2 (c^2)^{-1} + K_{E21}^+ (c_{o3}^2)^2 (c^2)^2}{c_{o3}^2},
\]

### Table 13. Values of the limit \( Y_{03}^+ \) of the partial molar electro-optical absorption of TCNE in solutions of HMB and TCNE in CCl₄ at 298.15 K.

<table>
<thead>
<tr>
<th>( c_{o3}^0/\text{mol m}^{-3} )</th>
<th>8.134</th>
<th>23.972</th>
<th>32.097</th>
<th>52.375</th>
<th>113.262</th>
<th>162.542</th>
<th>360.880</th>
<th>371.884</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{03}^+ (\tilde{\nu}, \chi)/10^{-19} \text{ m}^2 \text{V}^{-2} \text{mol}^{-1} )</td>
<td>156</td>
<td>2457</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td></td>
<td>156</td>
<td>2457</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td>( \tilde{\nu}/10^4 \text{m}^{-1} )</td>
<td>0</td>
<td>( \pi/2 )</td>
<td>0</td>
<td>( \pi/2 )</td>
<td>0</td>
<td>( \pi/2 )</td>
<td>0</td>
<td>( \pi/2 )</td>
</tr>
<tr>
<td>( \chi )</td>
<td>0</td>
<td>216</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>216</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>216</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>216</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>216</td>
<td>718</td>
<td>3211</td>
<td>765</td>
<td>3354</td>
<td>840</td>
<td>3515</td>
</tr>
</tbody>
</table>
where the indices "E" are used to designate quantities in an applied electric field. The quantities [36]

\[ L_{ij}^E = \lim_{E \to 0} \left( \frac{\partial \alpha_{E,j}}{\partial E_{ij}} \right) \]  

(55)

\[ q_j^E = \lim_{E \to 0} \left( \frac{\partial \alpha_{E,j}^q}{\partial E} \right) \]  

(56)

\[ p_{j\nu}^E = \lim_{E_{\nu} \to 0} \left( \frac{\partial K_{E,j}}{\partial E_{\nu}} \right) \]  

(57)

are introduced to describe the field dependence of the molar absorption coefficients \( \alpha_{E,j} \), the initial concentrations \( c_{E,j} \) of the substances used to generate the solution, and the equilibrium constants \( K_{E,j} \) of the occurring chemical reactions. With (54) to (57) follows from (53)

\[ Y_{ij}^{+} = \left[ 1 + K_{c_{11}^{+}}(c_{02}^{+})^{-1} + K_{c_{21}^{+}}(c_{02}^{+})^2(c_{02}^{+})^{-2} \right]^{-1} \]  

(58)

\[ \cdot \left\{ (L_{11}^{+} + q_1^{+})x_{11}^{+} K_{c_{11}^{+}} c_{02}^{+}(c_{02}^{+})^{-1} \right. 
\]
\[ + \left( L_{21}^{+} + q_2^{+} \right)x_{21}^{+} K_{c_{21}^{+}} (c_{02}^{+})^2(c_{02}^{+})^{-2} \]  

\[ + \left( p_{11}^{+} + q_1^{+} \right)(x_{11}^{+} - K_{00}) K_{c_{11}^{+}} c_{02}^{+}(c_{02}^{+})^{-1} \]  

\[ + \left( p_{21}^{+} + 2q_2^{+} \right)(x_{21}^{+} - K_{00}) K_{c_{21}^{+}} (c_{02}^{+})^2(c_{02}^{+})^{-2} \} \]  

In the last two terms of the second bracket are the partial molar absorptions \( \alpha_{E,j} \) which cause a rather complicated dependence of \( Y_{ij}^{+} \) on \( c_{02}^{+} \) and therefore the application of the formal expansion, Eq. (19), is not appropriate.

The quantities \( L_{ij}^{E}(\vec{r}, \chi) \) are related to the transition dipole moment \( \mu_{E,j} \) and to the electric dipole moments \( \mu_{E,j} \) and \( \mu_{E,j} \) and the polarizabilities \( \alpha_{E,j} \) and \( \alpha_{E,j} \) of the considered molecule \( A_j \) in its ground and excited electronic state as may be recognized from (III.6) to (III.20). An evaluation of the dependence of \( L_{ij}^{E} \) on \( \vec{r} \) and \( \chi \) leads to quantities \( D_{ij}^{*} \) of I* to I* compare (III.6) to (III.10). From \( D_{ij}^{*} \) to I* in favorable cases information about \( \mu_{E,j}, \mu_{E,j}, \alpha_{E,j}, \alpha_{E,j} \), and \( \alpha_{E,j} \) may be obtained.

For a value of \( q_j^{*} \) other than zero, two causes are mainly responsible. The first cause is the electrostriction of the solution in an electric field. An estimation leads to a contribution approximately equal to \( 1 \cdot 10^{-21} \) \( \text{V}^{-2} \text{m}^2 \), which can be neglected compared to the errors of measured values of \( L_{ij}^{E} \). The second cause is the diffusion exchange of molecules in parts of the solution outside of the applied electric field and in parts inside of the field. This contribution is even smaller at least if the frequency of the applied field is large enough. Therefore the quantities \( q_j^{*} \) and \( q_j^{*} \) may safely be neglected in (58).

A value of \( p_{j\nu}^{*} \) different from zero is caused by the electric field dependence of the Gibbs energy. According to (IV.33) and (IV.35) it is

\[ RT \ln K_{E,j}^{+} = - (g_{E,j}^{+} \gamma - \mu_{E,j}) \]  

(59)

where \( g_{E,j}^{+} \) is the model molar Gibbs energy of the substance \( A_j \) in the solution in an applied electric field, which can be represented as

\[ g_{E,j}^{+} = g_{j}^{+} - \frac{B_{i}^{E} N_{A}}{6} \]

\[ \cdot \left\{ (kT)^{-1} \phi_{E,j} \left( 1 - \frac{1}{j} \gamma_{E,j} \right)^{-2} \right. \]  

\[ \cdot \left\{ (kT)^{-1} \phi_{E,j} \left( 1 - \frac{1}{j} \gamma_{E,j} \right)^{-2} \right. \]  

\[ \cdot \left\{ (kT)^{-1} \phi_{E,j} \left( 1 - \frac{1}{j} \gamma_{E,j} \right)^{-2} \right. \]  

\[ \cdot \left\{ (kT)^{-1} \phi_{E,j} \left( 1 - \frac{1}{j} \gamma_{E,j} \right)^{-2} \right. \]  

\[ + \left( 1 - \frac{1}{j} \gamma_{E,j} \right)^{-1} \alpha_{E,j}^{2} \) \]  

(60)

With the values obtained in Sect. 4.3 the values of \( p_{i1}^{*} \) and \( p_{i1}^{*} \) are calculated as listed in Table 14.

Considering the quantities \( c_{02}^{+}, K_{c_{11}^{+}}, K_{c_{21}^{+}}, x_{11}^{+}, x_{21}^{+} \) and \( K_{00}^{+} \), whose values can be calculated using (19) and the data obtained in Sect. 4.1, as known quantities, and neglecting \( g_{E,j}^{+} \) and \( g_{j}^{+} \), analysis of variance according to (58) shows that the coefficients \( L_{11}^{+}, x_{11}^{+}, L_{21}^{+}, x_{21}^{+} \) and \( p_{11}^{+} \) may be estimated from usable data, but not the fourth coefficient \( p_{21}^{+} \) because this term has too small a value and causes a variation too small in the considered concentration interval of \( c_{02}^{+} \). Therefore the fourth term was taken into account with the above calculated value \( p_{11}^{+} = 50.9 \cdot 10^{-20} \text{V}^{-2} \text{m}^2 \) as known quantity. Multiple regression according to (58) leads to an estimator for \( p_{11}^{*} \), namely \( p_{11}^{*} = (102 \pm 6) \cdot 10^{-20} \text{V}^{-2} \text{m}^2 \). The excellent agreement of the calculated value, Table 14, and the estimated value support the theoretical models used for the evaluation of data and confirms the quality of the data obtained by electro-optical absorption measurements. Considering also the value \( p_{11}^{*} = 103.8 \cdot 10^{-20} \text{V}^{-2} \text{m}^2 \) as known, multiple re-

* Compare (131) [53], for example, after averaging over all orientations in the applied field.
The values of $L^*_{11}$ and $L^*_{21}$ at $\chi = 0$ of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K. The curves are calculated using (58) and the data in Tables 4, 5 and 14.

The regression according to (58) allows to estimate the values of $x^*_1 L^*_{11}$ and $x^*_2 L^*_{21}$ at $\chi = 0$ and $\pi/2$; they are represented in Figs. 4 and 5.

The values of $L^*_I x^*_I$ ($I = 11, 21$) depend on $\tilde{v}$ and $\chi$ according to (III.6). Multiple regression leads to the values of $D^*_I, \ldots, I^*_I$; they are listed in Table 14. The further evaluation is based on Eqs. (III.11) to (III.20). For the solvent CCl$_4$ the quantities $Q_i^{(0)} (E_i), i = 1, \ldots, 5$, can safely be neglected as well as $S^{(1)}$ and $S^{(2)}$ (an assumption confirmed by the very small value of $D^*_I$). Since the values of $L^*_I$ and $I^*_I$ and the values of $H^*_I$ and $I^*_I$ are almost equal, the dipole moments $\mu_{\text{a11}}$ and $\mu_{\text{a11}}$ and the transition dipole moment $\mu_{\text{a11}}$ (with $m = \mu_{\text{a11}}$) are at least nearly parallel to each other, a fact rather strongly confirming the assumed symmetry of the HMB-TCNE complex, namely a symmetry corresponding to the point group $C_{2v}$.

The values of $D^*_I, \ldots, I^*_I$ depend on $v$ and $l$ according to (III.6). Multiple regression leads to $L^*_I \sim 10^{-16} V^{-2} m^{-4} mol^{-1}$ (HMB)-TCNE ($J = 11$) and (HMB)$_2$-TCNE ($J = 21$).

The values of $D^*_I, \ldots, I^*_I$ depend on $v$ and $l$ according to (III.6). Multiple regression leads to $L^*_I \sim 10^{-16} V^{-2} m^{-4} mol^{-1}$ (HMB)-TCNE ($J = 11$) and (HMB)$_2$-TCNE ($J = 21$).

The values of $D^*_I, \ldots, I^*_I$ depend on $v$ and $l$ according to (III.6). Multiple regression leads to $L^*_I \sim 10^{-16} V^{-2} m^{-4} mol^{-1}$ (HMB)-TCNE ($J = 11$) and (HMB)$_2$-TCNE ($J = 21$).

![Fig. 4. Values of $L^*_I x^*_I$ and $L^*_I x^*_2$ at $\chi = 0$ of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K. The curves are calculated using (58) and the data in Tables 4, 5 and 14.](image)

![Fig. 5. Values of $L^*_I x^*_I$ and $L^*_I x^*_2$ at $\chi = 0$ of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K. The curves are calculated using (58) and the data in Tables 4, 5 and 14.](image)

### Table 14. Evaluation of the electro-optical absorption measurements for solutions in CCl$_4$ at $T = 298.15$ K.

<table>
<thead>
<tr>
<th>$J$</th>
<th>Remark</th>
<th>HMB-TCNE</th>
<th>(HMB)$_2$-TCNE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$11$</td>
<td>$p_j/10^{-20}$</td>
<td>$103.8$</td>
<td>$50.9$</td>
</tr>
<tr>
<td>$21$</td>
<td>$D^*_j/10^{-20}$</td>
<td>$40.7 \pm 5.1$</td>
<td>$9 \pm 8$</td>
</tr>
<tr>
<td>$E^*_j/10^{-20}$</td>
<td>$1216 \pm 30$</td>
<td>$120 \pm 80$</td>
<td></td>
</tr>
<tr>
<td>$F^*_j/10^{-40} CV^{-1}$</td>
<td>$496 \pm 16$</td>
<td>$91 \pm 30$</td>
<td></td>
</tr>
<tr>
<td>$G^*_j/10^{-40} CV^{-1}$</td>
<td>$480 \pm 16$</td>
<td>$69 \pm 30$</td>
<td></td>
</tr>
<tr>
<td>$H^*_j/10^{-60} C^2 m^2$</td>
<td>$690 \pm 230$</td>
<td>$960 \pm 210$</td>
<td></td>
</tr>
<tr>
<td>$L^*_j/10^{-60} C^2 m^2$</td>
<td>$620 \pm 230$</td>
<td>$860 \pm 210$</td>
<td></td>
</tr>
<tr>
<td>$R^*_j/10^{-10} V^{-1} m$</td>
<td>$1.12 \pm 0.14$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$R^*_j/10^{-10} V^{-1} m$</td>
<td>$1.26 \pm 0.68$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$(\alpha_{a} \beta_{a} \gamma_{a}/10^{-40} CV^{-1} m^2) + (\alpha_{a} \beta_{a} \gamma_{a} \gamma_{a} \gamma_{a})/10^{-40} CV^{-1} m^2$</td>
<td>$6.5 \pm 1.0$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$((\alpha_{a} \beta_{a} \gamma_{a} \gamma_{a})/10^{-40} CV^{-1} m^2) + (\alpha_{a} \beta_{a} \gamma_{a})/10^{-40} CV^{-1} m^2$</td>
<td>$6 \pm 6$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$\mu_{a} /10^{-30}$</td>
<td>$19.8 \pm 0.8$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$\mu_{a} /10^{-30}$</td>
<td>$24 \pm 4$</td>
<td>$22 \pm 4$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{a} \beta_{a} \gamma_{a} /10^{-40} CV^{-1} m^2$</td>
<td>$19.8 \pm 3.0$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{a} \beta_{a} \gamma_{a} \gamma_{a} \gamma_{a} /10^{-40} CV^{-1} m^2$</td>
<td>$89 \pm 30$</td>
<td>$-$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{a} \beta_{a} \gamma_{a} /10^{-40} CV^{-1} m^2$</td>
<td>$195 \pm 40$</td>
<td>$-$</td>
<td></td>
</tr>
</tbody>
</table>

**Remarks:**

1. Estimated from $F$ and $G$ assuming $\alpha_{a} \beta_{a} = \alpha_{a} \beta_{a}$.
2. Estimated from $H$ and $I$ assuming $\alpha_{a} \beta_{a} = \alpha_{a} \beta_{a}$.
3. Estimated from $F$, $G$, $H$ and $I$ with the presuppositions $\mu_{a} = 0$, $R_{011} = R_{011}$ and $R_{021} = R_{011}$.
Assuming \( \alpha_{ii} = \alpha_{ii} \), the value of the magnitude of the dipole moment \( \| \mu_{ii} \| \) in the excited state can be obtained from \( F_{ii}^* \) and \( G_{ii}^* \) and Eqs. (III.13) and (III.14) with a rather good accuracy and from \( H_{ii}^* \) and \( I_{ii}^* \) and Eqs. (III.15) and (III.16) with less accuracy. The data obtained, Table 14, agree within their errors. If there would be a 30% increase of the \( x \) and \( y \) components and an 120% increase of the \( z \) component of the polarizability during the excitation process (which corresponds to the changes estimated for the 2:1 complex), the estimated magnitude \( \| \mu_{ii} \| \) would be approximately 20% smaller. Hence one may expect a reliability of the reported value of \( \| \mu_{ii} \| \) of the same order.

Due to the intricate evaluation of data the quantities \( L_{ii}^* \) of the (HMB)\(_2\) TCNE complex are less accurate than the quantities \( E_{ii}^* \) of the HMB-TCNE complex as may be recognized from Figs. 4 and 5, and hence the quantities \( D_{ii}^* \), ..., \( I_{ii}^* \) are less reliable than the corresponding quantities \( D_{ii} \), ..., \( I_{ii} \). The values of \( D_{ii}^* \) and \( E_{ii}^* \) are almost zero within their errors as should be expected if the dipole moment of the 2:1 complex is zero. From the rather large values of \( H_{ii}^* \) and \( I_{ii}^* \) follows a rather large magnitude of the electric dipole moment \( \mu_{ii} \) of the 2:1 complex in its excited state. The equality of \( H_{ii}^* \) and \( I_{ii}^* \) shows that \( \mu_{ii} \) is parallel to the direction \( m_{ii} = \| \mu_{ii} \| / \| \mu_{ii} \| \) of the transition dipole moment. Assuming \( \alpha_{ii} = \alpha_{ii} \) leads to the value of \( \mu_{ii} \) as listed in Table 14. If there would be a 30% increase of the polarizability during the excitation process, the estimated value would be approximately 5% smaller. The small values of \( F_{ii} \) and \( G_{ii}^* \) confirm the very small value of the magnitude of the dipole moment in the electronic ground state: \( \| \mu_{ii} \| < 1 \cdot 10^{-30} \text{ Cm} \) (compare Section 4.3).

With the presuppositions \( \mu_{ii}^* = 0 \), \( R_{ii}^{(1)} = R_{ii}^{(3)} \), \( R_{ii}^{(2)} = R_{ii}^{(3)} \), and \( R_{ii}^{(2)} = R_{ii}^{(3)} \), \( F_{ii}^* \), \( G_{ii}^* \), \( H_{ii}^* \) and \( I_{ii}^* \) the quantities \( \mu_{ii}^* \), \( \alpha_{ii} \), \( \alpha_{ii}^* \), and \( \alpha_{ii} \) can be estimated; the values are listed in Table 14. The dipole moment \( \mu_{ii} \) of the 2:1 complex in the excited state is nearly equal to the change \( \mu_{ii} - \mu_{ii} \) of the dipole moment observed for the 1:1 complex. There may be a rather small increase of the \( x \) and \( y \) components of the polarizability (20%) and a larger increase of the \( z \) component (100%) during the considered excitation process, but due to their large errors these values are not very reliable.

Assuming model I — the formation of only the 1:1 complex — a modification of (58) can be obtained similarly as above, which allows the determination of \( L_{ii}^* \) and \( p_{ii} \) and two further coefficients describing the electric field dependence of \( \eta_{ii} \) and \( \lambda_{ii} \). Similar to the discussion in Sect. 4.1 it can be shown that the coefficients estimated from measured data differ strongly from the coefficients calculated from equations based on (31) and (37), respectively. Hence also the data of optical-absorption measurements confirm model I but contradict model II. The estimations of the field dependences of \( \eta_{ii} \) and \( \lambda_{ii} \) based on (31) and (37), respectively, furthermore show that the corresponding coefficients are negligibly small compared to \( L_{ii}^* \) and \( p_{ii} \).

The first determination of an electric dipole moment of an EDA complex in its excited state was done by Czeka and Meyer [61] using the results of electro-optical emission measurements. The results of electro-optical absorption measurements reported by Varma and Osterhoff [62] do not lead to any reliable data for EDA complexes. This may be recognized by the fact that from nine sets of data in three cases a negative value of \( \mu^2 \) was obtained, whose order of magnitude were almost the same as in the other cases. Some further preliminary results were communicated by Eckhardt [63] and by Liptay [53]. The reported magnitude \( \| \mu_{ii} \| = 32 \cdot 10^{-30} \text{ Cm} \) of the dipole moment of HMB-TCNE in its excited state [53] was much larger than the value obtained in this investigation, what is caused mainly by the usage of the erroneous value for the magnitude of the ground state dipole moment [16]. Groenen and van Velzen [64] reported the values

\[
D_{ii} = 39 \cdot 10^{-20} \text{ V}^{-2} \text{ m}^2, \\
E_{ii} = 746 \cdot 10^{-20} \text{ V}^{-2} \text{ m}^2, \\
F_{ii} = 223 \cdot 10^{-40} \text{ CV}^{-1} \text{ m}^2, \\
G_{ii} = 193 \cdot 10^{-40} \text{ CV}^{-1} \text{ m}^2, \\
H_{ii} = 568 \cdot 10^{-60} \text{ C}^2 \text{ m}^2, \\
I_{ii} = 590 \cdot 10^{-60} \text{ C}^2 \text{ m}^2
\]

for the HMB-TCNE complex. Since these authors considered only the formation of the 1:1 complex, the deviations to the values reported in this paper may be due to contributions of the 2:1 complex. But they also neglected the contributions caused by the field dependence of the equilibrium constants, i.e. they implicitly assumed \( p_{ii}^* = 0 \) (and naturally \( p_{ii} = 0 \)), what is a further reason for the deviations of the above data from those in Table 14.
5. Discussion

The data obtained by measurements of the optical absorptions, the densities, the refractive indices, the permittivities and the electro-optical absorptions could be interpreted by model I — i.e. formation of the HMB-TCNE and the (HMB)\textsubscript{2}-TCNE complex — as well as by model II — i.e. formation of only the HMB-TCNE complex. A decision between the two models is possible if the coefficients describing the solvent dependence of the activity effects ($\eta_{c11,10}$), the model molar absorption coefficients ($\lambda_{c11,10}$), the model molar refractions ($\lambda_{c211,10}$), the model molar electric susceptibilities ($\lambda_{c211,10}$) and the coefficients describing the electric field dependence of $\eta_{c11,10}$ and $\lambda_{c211,10}$ are calculated. For this, a suitable model is needed, and the obtained values are compared with those estimated from the experimental data. The results reported in Sect. 4.1 to 4.4 show that all measurements confirm model I but contradict model II. Hence for all further discussions only model I will be considered.

From the electro-optical absorption measurements it can be concluded that the HMB-TCNE complex exhibits, at least approximately, the symmetry of the point group $C_{2v}$. The transition dipole moment $\mu_{c11}$ is parallel to the two-fold rotation axis of the complex, and hence the first excited state, corresponding to the excitation at $\tilde{v} = 186 \cdot 10^4$ m\(^{-1}\), is a $\Lambda_1$ state as well as the ground state of the complex. The magnitude of the electric dipole moment is $|\mu_{c11}| = 7.0 \cdot 10^{-30}$ Cm in the ground state, the direction of $\mu_{c11}$ is from the donor HMB to the acceptor TCNE. The magnitude of the dipole moment is $|\mu_{c11}| = 19 \cdot 10^{-30}$ Cm in the considered excited state, and the directions of $\mu_{c11}$ and $\mu_{a11}$ are equal. Since there is a rather strong increase of the dipole moment during the excitation process, the electron-donor-acceptor absorption band may also be called, as is usual, a charge-transfer band. The dipole moment in the excited state is still much smaller than would be expected if the charge of an electron is transferred from the donor HMB to the acceptor TCNE ($54.5 \cdot 10^{-30}$ Cm, if the distance between the donor and the acceptor group is assumed to be $3.4 \cdot 10^{-10}$ m).

The (HMB)\textsubscript{2}-TCNE complex exhibits an optical absorption band with maximum at $184 \cdot 10^4$ m\(^{-1}\) in the same wavenumber interval as the HMB-TCNE complex and an integral absorption which is almost twice as large as that of the HMB-TCNE complex. The electric dipole moment of the (HMB)\textsubscript{2}-TCNE complex in its electronic ground state is either zero or nearly zero ($|\mu_{c21}| < 1 \cdot 10^{-30}$ Cm), a fact which confirms a sandwich-type configuration HMB-TCNE-HMB. The symmetry of the molecule in the ground state corresponds approximately to the point group $C_{2v}$, if there is a dipole moment different from zero, or to the point group $D_{2h}$, if the dipole moment is zero. Surprisingly the 2:1 complex has a dipole moment in the considered excited state, whose magnitude is nearly equal to the magnitude of the change of the dipole moment of the 1:1 complex; its direction is also parallel to the transition dipole moment and therefore parallel to the $z$ axis passing the centers of the groups HMB, TCNE and HMB. If the symmetry corresponds approximately to the point group $D_{2h}$, in the isolated 2:1 complex there have to be two close-spaced excited states corresponding to the irreducible representations $B_{1u}$ and $B_{1g}$. The interaction with the applied electric field and also with the surrounding solvent molecules causes a mixing of both states, which leads to a Franck-Condon state with a permanent electric dipole moment different from zero. The relaxation process associated with the transition from the Franck-Condon excited state to the equilibrium excited state (equilibrium with respect to the positions of nuclei of the complex and the surrounding solvent molecules) causes a decrease of the symmetry of the 2:1 complex, and probably the equilibrium excited state will correspond to the irreducible representation $A_1$ of the point group $C_{2v}$. Presuppositions for this interpretation are the existence of weak interactions between the HMB molecules and the central TCNE molecule in the complex and very weak interactions among both HMB molecules. These assumptions are supported by the following facts: (1) the considered absorption band of the 2:1 complex is very similar to the absorption band of the 1:1 complex but with an almost twice as large intensity, (2) the changes of the dipole moments during the excitation process are nearly equal for both complexes, and (3) the value of the standard reaction enthalpy $\Delta_{R}^{o}H^{*}$ for the 2:1 complex is approximately twice the value for the 1:1 complex.

The electrostatic interactions between solute molecules and the surrounding solvent molecules cause a shift of the absorption band of the complexes in...
a solution relative to the band of the complexes in the gaseous state [54]. With the data estimated in this investigation, the shift is $\Delta \tilde{\nu} = -4.6 \cdot 10^4 \text{ m}^{-1}$ for the 1:1 complex and $\Delta \tilde{\nu} = -2.9 \cdot 10^4 \text{ m}^{-1}$ for the 2:1 complex. Due to these small shifts, the absorption bands of both complexes, observed in CCl$_4$

in the same wavenumber interval, will be expected in the gaseous state also to be in one, but blue-shifted wavenumber interval.

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