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 CCl_4. 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 soluted in cyclohexane. Dielectric measurements of Briegleb, 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

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molecule of approximately $1 \cdot 10^5\,\mathrm{m}^{-1}$, additive to the red shift caused by dispersion interactions between the complex molecule and the surrounding solvent molecules. If the corresponding 2:1 complex 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 complex relative to the 1:1 complex of approximately $1 \cdot 10^5\,\mathrm{m}^{-1}$, 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 molecule with the solvent [19—26], self-association of a donor molecule with another one or of an acceptor molecule with another one [27], existence of different but stoichiometrical identical complexes [28], contact-charge-transfer interaction [28], activity coefficients of the educts and products significantly different from the value one [20, 29—32] and a dependence of the molar absorption coefficient on the composition of the solution [6, 9].

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 macroscopic phases and is intimately related to the problem of the determination of molecular quantities from such measurements. In paper I of this series we investigated the relations between bulk quantities, which can be measured on macroscopic systems, and molecular quantities, which have to be introduced by some theoretical model [36]. In paper 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 hexamethylbenzene (HMB, A_2) with the electron acceptor tetracyanoethylene (TCNE, A_3) have been investigated repeatedly [5, 12, 15—17, 23, 40—45]. The solvent chosen in our studies was carbon tetrachloride (A_1), because its molecules own neither an electric dipole moment nor a quadrupole moment and hence this solvent is very suited for permittivity and electro-optical absorption measurements; furthermore, in carbon tetrachloride the maximal solubility of the acceptor A_3 (approximately $(c_{03})_{\max} = 0.5\,\mathrm{mol\,m^{-3}}$) is much larger than in aliphatic hydrocarbons, and the maximal solubility of the donor A_2 (approximately $(c_{02})_{\max} = 750\,\mathrm{mol\,m^{-3}}$) is also rather large.

Measured were the mass densities ϱ, the optical absorption coefficients a, the relative permittivities ε_r, the refractive indices n and the derivatives

$$M = \lim_{E_\mathrm{a}^2 \to 0} (\partial a / \partial E_\mathrm{a}{}^2),$$

where E_a 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 $\mathsf{P}_{w\Phi}$, 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

$$\mathsf{P}_{wV} = 1/\varrho\,, \quad \mathsf{P}_{w\mathsf{K}} = a/\varrho\,, \quad \mathsf{P}_{w\mathsf{Z}} = (\varepsilon_\mathrm{r} - 1)/\varrho\,,$$
$$\mathsf{P}_{w\mathsf{Z}'} = (n^2 - 1)/\varrho \quad \text{and} \quad \mathsf{P}_{w\mathsf{Y}} = M/\varrho\,.$$

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

$$\begin{aligned} \mathsf{P}_{w\Phi} = \mathsf{P}_{w\Phi}^{+} &+ (M_3^{-1}\,\Phi_{03}^{+} - \mathsf{P}_{w\Phi}^{+})\,w_{03} \\ &+ [M_1^{-1}\,\Lambda_{w\Phi 1.2}^{+}(1 - w_{02}^{+}) \\ &\quad + M_2^{-1}\,\Lambda_{w\Phi 2.2}^{+}\,w_{02}^{+} \\ &\quad + M_3^{-1}\,\Lambda_{w\Phi 3.1}^{+}]\,w_{03}^{2} + \cdots, \end{aligned} \tag{1}$$

where M_1, M_2 and M_3 are the molar masses of A_1, A_2 and A_3, respectively, and $\Phi_{0J} = (\partial\Phi/\partial n_{0J})_{n_{0J'},\,\vartheta,}$ is the partial molar quantity of the substance A_J adjoint to the extensive quantity $\Phi = \mathsf{P}_{w\Phi}\,m_0$ 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.

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* The abbreviations Eq. (I....), ..., (IV....) signify equations of paper I, ..., IV of this series [36—39].

The quantities $\Lambda^{+}_{w\Phi J.\alpha}$ are the coefficients of the expansion

$$\Phi_{0J} = \Phi^{+}_{0J} + \sum_{\alpha=1}^{\infty} \Lambda^{+}_{w\Phi J.\alpha} w^{\alpha}_{03}\,, \tag{2}$$

as defined by (I.40), (I.46) and (I.47).

From a set of data $\mathrm{D_p} = \{(\mathsf{P}_{w\Phi}, w_{03};\, w^{+}_{02})_{\mathrm{s}}\}$ with a fixed value of w^{+}_{02}, 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 $\mathsf{P}^{+}_{w\Phi}$, Φ^{+}_{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 $\mathsf{P}^{+}_{w\Phi}$ and Φ^{+}_{03} can be estimated and all further coefficients $\Lambda^{+}_{w\Phi J.\alpha}$ have to be assumed negligibly small. The partial molar quantities Φ^{+}_{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 the change of the absorption coefficient or of other bulk quantities with varying composition of dilute solutions. Any equilibrium constant which might be determined under such conditions is an average of equilibrium constants corresponding to chemical reactions between individual species, as can be recognized from (IV.64) and (IV.75), for example. Similarly, the values of model molar quantities of individual species cannot be determined, but instead only some averages of those quantities; compare (IV.59) and (IV.70), 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:

$$\lambda\,\mathrm{A}_2 + \nu\,\mathrm{A}_3 \rightleftharpoons \mathrm{A}_{\lambda\nu}\,, \tag{3}$$
$$\lambda = 0, 1, 2, \ldots; \quad \nu = 0, 1, 2, \ldots; \quad \lambda = \nu \neq 0\,,$$
$$\lambda = \nu - 1 \neq 0\,, \quad \lambda - 1 = \nu \neq 0\,.$$

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 $\nu \neq 0$) as well as associations of donor molecules among themselves ($\lambda \geqq 2$, $\nu = 0$) and of acceptor molecules among themselves ($\lambda = 0$, $\nu \geqq 2$). Equation (3) corresponds to (IV.1) with $R = \lambda\nu$, $\nu_{R2} = -\lambda$, $\nu_{R3} = -\nu$ and $\nu_{RJ} = 1$ for $J \geqq 4$. 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 ($\lambda = 1$, $\nu = 1$) and of the 2:1 complex ($\lambda = 2$, $\nu = 1$).

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

The equilibrium constants $K^{*}_{\psi\lambda\nu}$ corresponding to the hypothetical chemical reactions (3) are related to the quantities $K_{\psi\lambda\nu}$ according to (IV.32) and (IV.36) as

$$K^{*}_{\psi\lambda\nu}(1 + F_{\psi\lambda\nu}) = K_{\psi\lambda\nu} = \frac{\psi_{\lambda\nu}}{\psi_2^{\lambda}\,\psi_3^{\nu}}\,(\psi^{\ominus})^{\lambda+\nu-1}, \tag{4}$$

where ψ_J is the value of the concentration variable of substance A_J ($J = 2, 3, \lambda\nu$) in the equilibrium state as defined by (I.72):

$$\psi_J = n_J/\chi_J \Psi\,. \tag{5}$$

n_J is the amount of the substance A_J present in the solution, Ψ is an extensive quantity and χ_J a constant, possibly different for different substances A_J; examples are listed in Table 1 of the first paper [36]. $\psi^{\ominus}$ is a standard quantity with an arbitrary value and a unit equal to the one of ψ_J. The quantity $F_{\psi\lambda\nu}$ as defined by (IV.34) describes the activity effects. It is related to the activity coefficients $\check{f}_{\psi J}$, defined by (I.132) and (I.133), as

$$F_{\psi\lambda\nu} = \frac{\check{f}^{\lambda}_{\psi 2}\,\check{f}^{\nu}_{\psi 3}}{\check{f}_{\psi\lambda\nu}} - 1\,. \tag{6}$$

According to (IV.39) a power-series expansion in ψ_{02} and ψ_{03} is possible:

$$\begin{aligned} F_{\psi\lambda\nu} = {} & \eta_{\psi\lambda\nu.10}\,\psi_{02} + \eta_{\psi\lambda\nu.01}\,\psi_{03} \\ & + \eta_{\psi\lambda\nu.11}\,\psi_{02}\,\psi_{03} + \eta_{\psi\lambda\nu.20}\,\psi_{02}^{2} + \cdots, \end{aligned} \tag{7}$$

such that $\lim_{n_0 \to n_{01}} F_{\psi\lambda\nu} = 0$, where $n_0 = n_{01} + n_{02} + n_{03}$ and n_{0J} is the initial amount of the pure substance A_J used to generate the solution. The ψ_J's are related to the concentration variables ψ_{0J},

$$\psi_{0J} = n_{0J}/\chi_J \varPsi\,, \tag{8}$$

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

$$\psi_2 = \psi_{02} - \chi_2^{-1} \sum_\lambda \sum_\nu \lambda\, \xi_{\psi\lambda\nu}\,, \tag{9}$$

$$\psi_3 = \psi_{03} - \chi_3^{-1} \sum_\lambda \sum_\nu \nu\, \xi_{\psi\lambda\nu}\,, \tag{10}$$

$$\psi_{\lambda\nu} = \chi_{\lambda\nu}^{-1} \xi_{\psi\lambda\nu}\,, \tag{11}$$

where $\xi_{\psi\lambda\nu}$, as defined by (IV.5), is the extent of the reaction (3) in a unit equal to that of $\chi_I \psi_{0I}$.

Any generalized density $\mathsf{P}_{\psi\varPhi} = \mathsf{P}_{w\varPhi} m_0/\varPsi$ is related to the corresponding model molar quantities φ_J (MMQ's) according to (IV.11) as

$$\mathsf{P}_{\psi\varPhi} = \sum_{I=1}^{3} \chi_I \psi_{0I} \varphi_I + \sum_{\lambda\nu} \xi_{\psi\lambda\nu} \varDelta_{\lambda\nu}\varphi\,, \tag{12}$$

where, as defined by (IV.12),

$$\varDelta_{\lambda\nu}\varphi = \varphi_{\lambda\nu} - \lambda\varphi_2 - \nu\varphi_3\,. \tag{13}$$

The dependence of any φ_J on the composition of the phase can be represented by power-series expansion in ψ_{02} and ψ_{03} as introduced in (I.84), or

$$\begin{aligned} \varphi_J = \varphi_J^* &+ \lambda_{\psi\varphi J.10}\, \psi_{02} + \lambda_{\psi\varphi J.01}\, \psi_{03} \\ &+ \lambda_{\psi\varphi J.11}\, \psi_{02}\psi_{03} + \lambda_{\psi\varphi J.20}\, \psi_{02}^2 + \cdots, \\ J &= 1, 2, 3 \text{ or } \lambda\nu\,, \end{aligned} \tag{14}$$

and similarly

$$\begin{aligned} \varDelta_{\lambda\nu}\varphi = \varDelta_{\lambda\nu}\varphi^* &+ \varDelta_{\lambda\nu}\lambda_{\psi\varphi.10}\, \psi_{02} \\ &+ \varDelta_{\lambda\nu}\lambda_{\psi\varphi.01}\, \psi_{03} + \cdots. \end{aligned} \tag{15}$$

The MMQ's φ_J are related to the PMQ's $\varPhi_{0J}$ as shown in (IV.14), or

$$\begin{aligned} \varPhi_{03} = \varphi_3 &+ \frac{1 - \chi_3 \psi_{03} \varPsi_{03}}{\chi_3} \sum_{I=1}^{3} \chi_I \psi_{0I} \left(\frac{\partial\varphi_I}{\partial\psi_{03}}\right)_{n_{03}',\, \vartheta_\iota} \\ &+ \varPsi_{03} \sum_{\lambda\nu} \xi_{\psi\lambda\nu} \varDelta_{\lambda\nu}\varphi + \frac{1 - \chi_3 \psi_{03} \varPsi_{03}}{\chi_3} \\ &\cdot \sum_{\lambda\nu} \left(\frac{\partial(\xi_{\psi\lambda\nu} \varDelta_{\lambda\nu}\varphi)}{\partial\psi_{03}}\right)_{n_{03}',\, \vartheta_\iota} \end{aligned} \tag{16}$$

and similarly for $\varPhi_{02}$. From (16) follows the limit $\varPhi_{03}^+$ for $\psi_{03} \to 0$ at a fixed value of n_{02}/n_{01}:

$$\begin{aligned} \varPhi_{03}^+ = \lim_{\psi_{03} \to 0} \varPhi_{03} = \varphi_3^+ &+ \chi_3^{-1} \sum_{I=1}^{2} \chi_I \psi_{0I}^+ \left(\frac{\partial\varphi_I}{\partial\psi_{03}}\right)_{n_{03}'}^+ + \varPsi_{03}^+ \sum_{\lambda\nu} \xi_{\psi\lambda\nu}^+ \varDelta_{\lambda\nu}\varphi^+ \\ &+ \chi_3^{-1} \sum_{\lambda\nu} \left[\left(\frac{\partial\xi_{\psi\lambda\nu}}{\partial\psi_{03}}\right)_{n_{03}'}^+ \varDelta_{\lambda\nu}\varphi^+ + \xi_{\psi\lambda\nu}^+ \left(\frac{\partial\varDelta_{\lambda\nu}\varphi}{\partial\psi_{03}}\right)_{n_{03}'}^+ \right]. \end{aligned} \tag{17}$$

According to (I.18) and (I.19), the following relation holds true:

$$\begin{aligned} \left(\frac{\partial\gamma}{\partial\psi_{03}}\right)_{n_{03}'}^+ &= \left(\frac{\partial\gamma}{\partial\psi_{03}}\right)_{\psi_{03}'}^+ + \frac{\chi_3 \varPsi_{03}^+ \varPsi^+}{\varPsi_{01}^+} \left(\frac{\partial\gamma}{\partial n_{01}}\right)_{n_{01}}^+, \\ \gamma &= \varphi_I, \varDelta_{\lambda\nu}\varphi, \xi_{\psi\lambda\nu}\,. \end{aligned} \tag{18}$$

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

$$\varPhi_{03}^+ = \frac{B_{\varPhi 0} + B_{\psi\varPhi 1}\psi_{02}^+ + B_{\psi\varPhi 2}(\psi_{02}^+)^2 + \cdots}{1 + A_{\psi 1}\psi_{02}^+ + A_{\psi 2}(\psi_{02}^+)^2 + \cdots}\,, \tag{19}$$

where

$$A_{\psi 1}\psi^\ominus = \chi_3^{-1} \chi_{11} K_{\psi 11}^*\,, \tag{20}$$

$$A_{\psi 2}(\psi^\ominus)^2 = \chi_3^{-1} \{\chi_{21} K_{\psi 21}^* + \chi_{11} K_{\psi 11}^* (\eta_{\psi 11.10} - 2\,\chi_2^{-1} \chi_{20} K_{\psi 20}^*)\}\,, \tag{21}$$

$$B_{\varPhi 0} = \varphi_3^* + \chi_3^{-1} \varPsi_{01}^{*-1} \lambda_{\psi\varphi 1.01} = \varPhi_{03}^*\,, \tag{22}$$

$$B_{\psi\varPhi 1} = A_{\psi 1}(\varphi_3^* + \chi_3^{-1} \varPsi_{01}^{*-1} \lambda_{\psi\varphi 1.01} + \varDelta_{11}\varphi^*) + C_1 - \chi_3^{-1} \varPsi_{01}^{*-1} \chi_2 \varPsi_{02}^* \lambda_{\psi\varphi 1.01}\,, \tag{23}$$

$$\begin{aligned} B_{\psi\Phi 2} = {} & A_{\psi 2}(\varphi_3^* + \chi_3^{-1}\Psi_{01}^{*-1}\lambda_{\psi\varphi 1.01} + \Delta_{21}\varphi^*) \\ & + A_{\psi 1}[(\eta_{\psi 11.10} - 2\,\chi_2^{-1}\chi_{20}K_{\psi 20}^*)(\psi^{\ominus})^{-1}(\Delta_{11}\varphi^* - \Delta_{21}\varphi^*) + C_1 + \Delta_{11}\lambda_{\psi\varphi 10} \\ & \qquad - \chi_3^{-1}\Psi_{01}^{*-1}\chi_2\Psi_{02}^*\lambda_{\psi\varphi 1.01} - 2\,\chi_2^{-1}\chi_{20}K_{\psi 20}^*(\psi^{\ominus})^{-1}\Delta_{20}\varphi^*] \\ & - \chi_3^{-1}\Psi_{01}^{*-1}[\chi_2\Psi_{02}^*(\lambda_{\psi\varphi 1.11} - \chi_3\Psi_{03}^*\lambda_{\psi\varphi 1.10}) + \chi_3\Lambda_{\psi\Phi 3.10}\lambda_{\psi\varphi 1.10} \\ & \qquad + (\Psi_{01}^{*-1}\Lambda_{\psi\Phi 1.20} + \chi_2\Lambda_{\psi\Phi 2.10})\lambda_{\psi\varphi 1.01}] \\ & + \chi_3^{-1}\chi_{20}K_{\psi 20}^*(\psi^{\ominus})^{-1}[\Delta_{20}\lambda_{\psi\varphi 01} + \eta_{\psi 20.01}(\psi^{\ominus})^{-1}\Delta_{20}\varphi^* - \chi_3\Psi_{03}^*\Delta_{20}\varphi^*] + C_2\,, \end{aligned} \tag{24}$$

where

$$\begin{aligned} C_k = {} & \lambda_{\psi\varphi 3.k0} + \chi_3^{-1}\Psi_{01}^{*-1}(\lambda_{\psi\varphi 1.k1} - k\,\chi_3\Psi_{03}^*\lambda_{\psi\varphi 1.k0}) \\ & + \chi_3^{-1}\chi_2[\lambda_{\psi\varphi 2.(k-1)1} - (k-1)\,\chi_3\Psi_{03}^*\lambda_{\psi\varphi 2.(k-1)0}]\,. \end{aligned} \tag{25}$$

The further coefficients $B_{\psi\Phi 3}, B_{\psi\Phi 4}, \ldots$ 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 $\psi_{02} \to 0\,(\psi_{03} \to 0)$ with a fixed value of n_{01}. The quantity $B_{\Phi 0}$ is equal to the limit Φ_{03}^* 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 $A_{\psi 1}\psi_{02}^+ + A_{\psi 2}(\psi_{02}^+)^2 + \cdots \ll 1$, i.e. at sufficiently low concentration ψ_{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 an 1:1 complex may be satisfied but the apparent value of the equilibrium constant is actually related to the value of $A_{\psi 1} - B_{\psi\Phi 1}/B_{\psi\Phi 1}$ as was recognized by Hayman [33]. Since $B_{\psi\Phi 2}/B_{\psi\Phi 1}$ may be different for different specific quantities $\mathsf{P}_{w\Phi}$, 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 $B_{\psi\Phi 2}$ is possible only if for some of the investigated solutions $A_{\psi 1}\varphi_{02}^+$ 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 $\{(\Phi_{03}^+, w_{02}^+)_s\}$ according to (19) may lead to estimators for

$$A_{\psi 1}, A_{\psi 2}, \ldots, B_{\Phi 0}, B_{\psi\Phi 1}, B_{\psi\Phi 2}, \ldots,$$

as will be shown in Section 4.1.

Equations (20) and (21) show that only the equilibrium constant $K_{\psi 11}^*$ 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 $(\mathrm{HMB})_2$-TCNE as well as by $\eta_{\psi 11.10}$, describing an activity effect on the formation of the 1:1 complex in first order, or by the formation of the dimere $(\mathrm{HMB})_2$. 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 $K_{\psi 20}^* = 0$.

A further evaluation of the quantities $B_{\psi\Phi\alpha}$ can lead to the MMQ's φ_{11}^* and φ_{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 φ_2^* and φ_3^* and of the coefficients $\lambda_{\psi\varphi J.\alpha_2\alpha_3}$ as introduced in (14). The quantities φ_2^* and φ_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]; φ_3^* can also follow from $B_{\Phi 0}$. The quantities $\lambda_{\psi\varphi J.\alpha_2\alpha_3}$ 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_2O, dried with $CaCl_2$ and P_2O_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 spectralphotometer 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 w_{02}^{+} of HMB were measured, each set consisting of a few solutions with variable values of the mass fraction w_{03} of TCNE ($c_{02}^{+} = 7$ to $700\ \mathrm{mol\ m^{-3}}$, $c_{03} = 0.1$ to $1\ \mathrm{mol\ m^{-3}}$). Analysis of variance (F- and t-test) of the data has shown that in the investigated concentration intervals the specific quantity $\mathsf{P}_{w\mathsf{K}} = a/\varrho$, where ϱ is the density of the solution, is linearly dependent on the mass fraction w_{03} and that in the investigated wavenumber interval $\tilde{\nu} = 15 \cdot 10^5$ to $25 \cdot 10^5\ \mathrm{m^{-1}}$, the limit of $\mathsf{P}_{w\mathsf{K}}$ for $w_{03} \to 0$ vanishes, i.e. $\mathsf{P}_{w\mathsf{K}}^{+} = 0$. Hence under this condition the limit K_{03}^{+} of the partial molar absorption of TCNE can be calculated according to (1) by $\mathsf{K}_{03}^{+} = a\, m_0/\varrho\, n_{03} = a/c_{03}$. The values of K_{03}^{+} were determined for ten solutions in $\mathrm{CCl_4}$ at 298.15 K at 51 wavenumbers and for twelve solutions at 283.15, 293.15 and 303.15 K at 6 wavenumbers in the interval $\tilde{\nu} = 15 \cdot 10^5$ to $25 \cdot 10^5\ \mathrm{m^{-1}}$. Some values of K_{03}^{+} are listed in Table 1 as examples.

Table 1. Values of the limit K_{03}^{+} of the partial molar absorption of TCNE for solutions of HMB and TCNE in $\mathrm{CCl_4}$ at 298.15 K.

$\tilde{\nu}/10^5\ \mathrm{m^{-1}}$	17	18	19	20	21	22
$c_{02}^{+}/\mathrm{mol\ m^{-3}}$	$\mathsf{K}_{03}^{+}/\mathrm{m^2\ mol^{-1}}$					
7.7372	191.5	247.7	257.1	225.1	166.0	105.3
29.413	306.2	395.3	407.9	355.5	262.3	167.3
30.721	309.4	399.6	412.3	358.8	265.3	169.1
53.033	347.4	448.1	459.8	398.9	294.8	189.1
91.446	383.2	492.8	502.5	433.4	320.7	206.4
129.79	405.1	520.5	528.0	453.5	335.9	217.3
270.14	448.4	574.8	577.5	491.7	364.9	237.7
339.53	460.7	590.1	591.1	502.1	372.8	243.2
589.28	486.4	622.0	619.6	523.7	389.3	255.2
654.65	490.0	626.8	624.2	527.1	392.0	256.9

Since in the considered wavenumber interval $\mathsf{P}_{w\mathsf{K}}^{+} = 0$ and therefore also $B_{\mathsf{K}0} = 0$ from Eq. (19) follows

$$\begin{aligned}\mathsf{K}_{03}^{+}/\psi_{02}^{+} = {} & B_{\psi\mathsf{K}1} - A_{\psi 1}\,\mathsf{K}_{03}^{+} + B_{\psi\mathsf{K}2}\,\psi_{02}^{+} \\ & - A_{\psi 2}\,\mathsf{K}_{03}^{+}\psi_{02}^{+} + B_{\psi\mathsf{K}3}(\psi_{02}^{+})^2 \\ & - A_{\psi 3}\,\mathsf{K}_{03}^{+}(\psi_{02}^{+})^2 + \cdots . \qquad (26)\end{aligned}$$

Considering $\mathsf{K}_{03}^{+}/\psi_{02}^{+}$ as a random variable in dependence on K_{03}^{+}, ψ_{02}^{+}, $\mathsf{K}_{03}^{+}\psi_{02}^{+}$, $(\psi_{02}^{+})^2$, $\mathsf{K}_{03}^{+}(\psi_{02})^2, \ldots$, analysis of variance (F- and t-test) and multiple regression lead to the number of coefficients significantly different from zero and to estimators for the coefficients $B_{\psi\mathsf{K}\alpha}$ and $A_{\psi\alpha}$. As concentration variables ψ_{02}^{+} were used c_{02}^{+}, w_{02}^{+}, x_{02}^{+} and r_{02}^{+} (compare Table 1 [36]); an example of the results using $\psi_{02}^{+} = c_{02}^{+}$ is shown in Table 2. From the results it may be recognized that the first four and only the first four coefficients of (26) are significantly different from zero with a statistical significance better than 95%. Multiple regression according to (26) assumes a random distribution of errors of $\mathsf{K}_{03}^{+}/\psi_{02}^{+}$, but accurate values not only of ψ_{02}^{+} but also of K_{03}^{+} and the latter assumption disagrees with experimental conditions. Hence the final values of the coefficients $A_{\psi 1}$, $A_{\psi 2}$, $B_{\psi\mathsf{K}1}$ and $B_{\psi\mathsf{K}2}$ were determined by iterative non-linear Gauss-Newton approximation using the values of the coefficients ob-

Table 2. Results of multiple regression according to (26), F- and t-test for absorption measurements at $\tilde{\nu} = 18 \cdot 10^5\ \mathrm{m^{-1}}$.

Number of coefficients assumed unequal zero	2	3	4	5
$B_{c\mathsf{K}1}/\mathrm{m^{-1}\ mol^{-2}}$	45.3 ± 8.5	56.4 ± 6.2	66.98 ± 0.35	66.87 ± 0.42
$t(B_{c\mathsf{K}1})$	10.6	18.0	382.4	315.1
$A_{c1}/\mathrm{m^3\ mol^{-1}}$	0.075 ± 0.017	0.106 ± 0.015	0.1511 ± 0.0013	0.1504 ± 0.0019
$t(A_{c1})$	8.9	13.9	236.6	155.3
$B_{c\mathsf{K}2}/\mathrm{m^2\ mol^{-3}}$		0.0190 ± 0.0078	0.497 ± 0.012	0.482 ± 0.033
$t(B_{c\mathsf{K}2})$		4.9	79.8	29.2
$A_{c2}/10^{-3}\ \mathrm{m^6\ mol^{-2}}$			0.722 ± 0.019	0.698 ± 0.054
$t(A_{c2})$			76.8	25.5
$B_{c\mathsf{K}3}/10^{-5}\ \mathrm{m^5\ mol^{-4}}$				-0.20 ± 0.41
$t(B_{c\mathsf{K}3})$				0.94
F		24.1	5897	0.9

Table 3. Best estimators for the coefficients $A_{\psi 1}$ and $A_{\psi 2}$ at 298.15 K.

ψ_J	$\psi^\ominus$	$A_{\psi 1}\,\psi^\ominus$	$A_{\psi 2}\,(\psi^\ominus)^2$
c_J	$1\ \mathrm{mol\,m^{-3}}$	0.15098 ± 0.00032	$(7.335 \pm 0.072) \cdot 10^{-4}$
w_J	1	1476.3 ± 3.2	71290 ± 690
x_J	1	1557.6 ± 3.3	79420 ± 770
r_J	1	1559.6 ± 3.3	80980 ± 770

tained from (26) as starting values and assuming a random distribution of errors of K_{03}^{+} and accurate values of ψ_{02}^{+}.

The values of the estimators $A_{\psi 1}$ and $A_{\psi 2}$ at different wavenumbers are equal within deviations as expected from the errors of the measured quantities. Averaging over all investigated wavenumbers leads to the best estimators as listed in Table 3.

With the estimated values for $A_{\psi 1}$ and $A_{\psi 2}$ and the values of K_{03}^{+} and ψ_{02}^{+}, the left-hand side of the following equation can be calculated:

$$\frac{\mathsf{K}_{03}^{+}(1 + A_{\psi 1}\,\psi_{02}^{+} + A_{\psi 2}\,(\psi_{02}^{+})^2)}{\psi_{02}^{+}} = B_{\psi \mathsf{K}1} + B_{\psi \mathsf{K}2}\,\psi_{02}^{+}\,. \tag{27}$$

Considering the left-hand side of (27) as a random variable in dependence on ψ_{02}^{+}, linear regression leads to the best estimators for $B_{\psi \mathsf{K}1}$ and $B_{\psi \mathsf{K}2}$; some examples choosing $\psi_{02}^{+} = c_{02}^{+}$ are listed in Table 4.

With the best estimators for $A_{\psi 1}$, $A_{\psi 2}$, $B_{\psi \mathsf{K}1}$ and $B_{\psi \mathsf{K}2}$, the quantity $(\mathsf{K}_{03}^{+})_{\mathrm{calc}}$ can be calculated according to (19). The relative errors $(\mathsf{K}_{03}^{+} - (\mathsf{K}_{03}^{+})_{\mathrm{calc}})/\mathsf{K}_{03}^{+}$ for the different solutions and wavenumbers are nearly always smaller than 0.005 and this magnitude agrees with the experimental errors of the absorption coefficients a. Hence the experimental data obtained from absorption measurements are completely described by the assumed model with the four coefficients $A_{\psi 1}$, $A_{\psi 2}$, $B_{\psi \mathsf{K}1}$ and $B_{\psi \mathsf{K}2}$ different from zero.

The value of the quantity $A_{\psi 1}$ is according to (20) directly related to the value of $K_{\psi 11}^{*}$ of the equilibrium constant of the formation of the 1:1 complex HMB-TCNE. For the interpretation of the quantity $A_{\psi 2}$ according to (21) the assumption $K_{\psi 20}^{*} = 0$ has to be introduced (compare Section 2.3). The value of $A_{\psi 2}$ is then caused by the equilibrium constant $K_{\psi 21}^{*}$ of the formation of the 2:1 complex (HMB)$_2$-TCNE and/or by the coefficient $\eta_{\psi 11.10}$, which describes according to (7) the first-order activity effect on the 1:1 complex formation. Assuming $\eta_{\psi 11.10} = 0$, it becomes

$$K_{\psi 21}^{*} = A_{\psi 2}\,\chi_3\,\chi_{21}^{-1}\,(\psi^\ominus)^2\,,$$

assuming $K_{\psi 21}^{*} = 0$ it will be $\eta_{\psi 11.10} = A_{\psi 2}/A_{\psi 1}$, the values are listed in Table 5.

If the assumption $\eta_{\psi 11.\alpha_1\alpha_2} = 0$ for $\alpha_1, \alpha_2 = 0, 1, 2, \ldots$, which is equivalent to $F_{\psi 11} = 0$, is met for one concentration variable $\psi_J^{(\mathrm{t})}$ it usually will not be true for another concentration variable $\psi_J^{(\mathrm{u})}$ as has been discussed at (IV.44). The relations between the coefficients $\eta_{\psi 11.10}$ are

$$\begin{aligned}\eta_{c11.10} &= \frac{M_2\,V_{01}^{*}}{M_1}\,\eta_{w11.10} + M_1\,V_{02}^{*} - M_2\,V_{01}^{*}\\ &= V_{01}^{*}\,\eta_{x11.10} + V_{02}^{*} - V_{01}^{*}\\ &= V_{01}^{*}\,\eta_{r11.10} + V_{02}^{*}\,.\end{aligned} \tag{28}$$

The values of $\eta_{\psi\lambda\nu.\alpha_1\alpha_2}$, which are different from zero for all but at least one concentration variable $\psi_J^{(\mathrm{t})}$, cause contributions to the estimators of $A_{\psi 1}$ and $A_{\psi 2}$ as listed in Table 3. Hence the values of K_{c11}^{*} and K_{c21}^{*}, for example, obtained from A_{c1} and A_{c2}, show some deviations from the values obtained from $K_{\psi 11}^{*}$ and $K_{\psi 21}^{*}$ $(\psi \neq c)$ using (IV.43) as may be seen from the data in Table 5, the deviations of K_{c21}^{*} are even larger if the contributions due to the term $K_{\psi 11}^{*}\,\eta_{\psi 11.10}$ 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

$\tilde{\nu}/10^5\ \mathrm{m^{-1}}$	$B_{c\mathsf{K}1}/10^{-3}\ \mathrm{m^{-1} \cdot mol^{-2}}$	$B_{c\mathsf{K}2}/10^{-5}\ \mathrm{m^{2} \cdot mol^{-3}}$	$\varkappa_{11}^{*}/\mathrm{m^2 \cdot mol^{-1}}$	$\varkappa_{21}^{*}/\mathrm{m^2 \cdot mol^{-1}}$
17	51618 ± 42	39486 ± 25	341.9 ± 0.8	538 ± 5
18	66827 ± 48	50367 ± 28	442.6 ± 1.0	687 ± 7
19	69646 ± 38	49667 ± 23	461.3 ± 1.0	677 ± 7
20	61180 ± 20	41588 ± 12	405.2 ± 0.9	567 ± 6
21	45089 ± 32	30986 ± 19	298.7 ± 0.7	422 ± 4
22	28558 ± 28	20474 ± 17	189.2 ± 0.5	279 ± 3

Table 4. Best estimators for the coefficients $B_{c\mathsf{K}1}$ and $B_{c\mathsf{K}2}$ and molar absorption coefficients of the complexes HMB-TCNE and (HMB)$_2$-TCNE in CCl$_4$ at 298.15 K.

[20, 24, 29, 30, 49—51]; the best choice would be that one, where the terms $\eta_{\psi\lambda\nu.\alpha_1\alpha_2}\,\psi_{02}^{\alpha_1}\,\psi_{03}^{\alpha_3}$ in (7) give the smallest contribution to $F_{\psi\lambda\nu}$. An analysis of variance (F-test and t-test) of the data according to (26) including the term $A_{\psi 3}\,\mathsf{K}_{03}^{+}(\psi_{02}^{+})^2$ on the right-hand side, does not lead to a statistically significant assertion even if the term seems to contribute the least for $\psi_{02}^{+} = c_{02}^{+}$; 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 concentration 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_{c11}^{*} 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 ($\pm t_{1-\alpha} s$, where s is the standard deviation of the mean and $\alpha = 0.025$).

For optical absorption measurements, where the density D_{Φ} was identified with the absorption coefficient a, the MMQ's φ_J^{*} occurring in (14) and (15) must, according to Sect. 9.4 of paper I, be identified with the molar absorption coefficient $\varkappa_J^{*}$ of substance A_J. Since in the considered wavenumber interval it is $\varkappa_1^{*} = \varkappa_2^{*} = \varkappa_3^{*} = 0$, one can assume $\lambda_{c\varkappa J.\alpha_2\alpha_3} = 0$, for $J = 1, 2, 3$; $\alpha_2 = 0, 1, 2, \ldots$; $\alpha_3 = 0, 1, 2, \ldots$, as has been discussed in paper I. Hence from (23) and (24), it follows that the molar absorption coefficients of the 1:1 complex are $\varkappa_{11}^{*} = B_{c\mathsf{K}1}/A_{c1}$; the values are listed in Table 4 and drawn in Figure 1. Assuming as above $K_{c20}^{*} = 0$ and $\eta_{c11.10} = 0$ it is

$$B_{c\mathsf{K}2} = A_{c2}(\varkappa_{21}^{*} - 2\varkappa_2^{*}) + A_{c1}\,\lambda_{c\varkappa 11.10}\cdot$$

$\lambda_{c\varkappa 11.10}$ describes according to Eq. (14) the solvent dependence of the molar absorption coefficient $\varkappa_{11}$ of the 1:1 complex in first-order relating to c_{02}. Assuming $\lambda_{c\varkappa 11.10} = 0$, then the molar absorption co. efficients $\varkappa_{21}^{*} = B_{c\mathsf{K}2}/A_{c2}$ 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

$$B_{c\mathsf{K}2} = A_{c1}(\varkappa_{11}^{*}\,\eta_{c11.10} + \lambda_{c\varkappa 11.10})$$

and the values of $\lambda_{c\varkappa 11.10}$ 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 complexes 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 $\lambda_{c\varkappa 11.10}$, which represents the solvent dependence of the molar absorption coefficient $\varkappa_{11}$ 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.

ψ_J $\psi^{\ominus}$	Remark	c_J 1 mol m^{-3}	w_J 1	x_J 1	r_J 1
$K_{\psi 11}^{*}$	1	0.15098 ± 0.00032	3346.6 ± 6.8	1557.6 ± 3.3	1559.6 ± 3.3
$K_{\psi 21}^{*}$	2	$(7.335 \pm 0.072) \cdot 10^{-4}$	251900 ± 2400	79420 ± 770	80980 ± 770
$\eta_{\psi 11.10}\,\psi^{\ominus}$	3	$(4.858 \pm 0.049) \cdot 10^{-3}$	48.29 ± 0.48	50.99 ± 0.51	51.92 ± 0.51
K_{c11}^{*}	4		0.15119 ± 0.00032	0.15121 ± 0.00032	0.15140 ± 0.00032
$K_{c21}^{*}/10^{-4}$	4		7.477 ± 0.071	7.485 ± 0.073	7.632 ± 0.073
$K_{c21}^{*}/10^{-4}$	5		7.592 ± 0.072	7.608 ± 0.073	7.902 ± 0.073
$\eta_{\psi 11.10}\,\psi^{\ominus}$	6	0	-0.7414 ± 0.0009	-0.8371 ± 0.0009	-1.8371 ± 0.0009

Remarks:
1. From the values $A_{\psi 1}$, Table 3.
2. From the values $A_{\psi 2}$, Table 3, assuming $K_{\psi 20}^{*} = 0$ and $\eta_{\psi 11.10} = 0$.
3. From the values $A_{\psi 1}$, $A_{\psi 2}$, Table 3, assuming $K_{\psi 20}^{*} = 0$ and $K_{\psi 21}^{*} = 0$.
4. Calculated from $K_{\psi 11}^{*}$ 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 $\eta_{\psi 11.10}$ $(\psi \neq c)$ as calculated 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 $\eta_{c11.10}$ and $\lambda_{c\varkappa 11.10}$ can be determined independently.

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

$$\eta_{c11.10} = \left(\frac{\partial F_{c11}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota} = \left(\frac{\partial \ln (\check{f}_{c2}\check{f}_{c3}/\check{f}_{c11})}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota}, \tag{29}$$

where $\check{f}_{cI}$ is the activity coefficient of the substance A_I defined by (I.132) and (I.133). From (I.136) follows

$$\left(\frac{\partial \ln \check{f}_{cI}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota} = \frac{1}{RT}\left[\left(\frac{\partial g_{\mathrm{m}I}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota} + V^*\left(\frac{\partial g_{\mathrm{m}2}}{\partial n_I}\right)_{n_{I'},\, \vartheta_\iota} + n_{01}\left(\frac{\partial}{\partial c_{02}}\left(\frac{\partial g_{\mathrm{m}1}}{\partial n_I}\right)_{n_{I'},\, \vartheta_\iota}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota}\right] + v_I^*\left(\frac{v_2^*}{V_{01}^{\mathrm{o}}} - 1\right) - \frac{\lambda_{cvI.10}}{V_{01}^{\mathrm{o}}}, \tag{30}$$

where $g_{\mathrm{m}I}$ 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_{01}^{o} is the molar volume of the pure solvent (CCl_4), v_I is the model molar volume of the substance A_I and $\lambda_{cvI.10}$ is one coefficient of the power-series (14) for $\varphi_I = v_I$. Application of (I.17) and introducing (30) into (29) leads to

$$\eta_{c11.10} = \frac{1}{RT}\left[\left(\frac{\partial g_{\mathrm{m}2}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota} + \left(\frac{\partial g_{\mathrm{m}3}}{\partial c_{02}}\right)_{n_{01},\, c_{03},\, \vartheta_\iota} - \left(\frac{\partial g_{\mathrm{m}11}}{\partial c_{02}}\right)_{n_{01},\, c_{03},\, \vartheta_\iota}\right] + (v_{11}^* - v_2^* - v_3^*)(1 - v_2^*/V_{01}^{\mathrm{o}}) + (1/V_{01}^{\mathrm{o}})(\lambda_{cv11.10} - \lambda_{cv2.10} - \lambda_{cv3.10}). \tag{31}$$

The quantities $g_{\mathrm{m}I}$ 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 $g_{\mathrm{m}I}$, which is at least a rough approximation for the considered dilute solutions, $g_{\mathrm{m}I}$ can be represented by [52]

$$g_{\mathrm{m}I} = g_{\mathrm{m}I}^* - \frac{N_{\mathrm{A}}}{2}\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}I}\{[1 - \mathbf{f}_I(\varepsilon_{\mathrm{r}})\,\boldsymbol{\alpha}_{\mathrm{g}I}]^{-1}\mathbf{f}_I(\varepsilon_{\mathrm{r}}) - [1 - \mathbf{f}_I(\varepsilon_{\mathrm{r}}^*)\,\boldsymbol{\alpha}_{\mathrm{g}I}]^{-1}\mathbf{f}_I(\varepsilon_{\mathrm{r}}^*)\}\,\boldsymbol{\mu}_{\mathrm{g}I}, \tag{32}$$

where N_{A} is the Avogadro constant, $\boldsymbol{\mu}_{\mathrm{g}I}$ and $\boldsymbol{\alpha}_{\mathrm{g}I}$ are the electric dipole moment and the polarizability of a molecule A_I (in the electronic ground state) and ε_{r} is the relative permittivity of the solution with the value $\varepsilon_{\mathrm{r}}^*$ of the pure solvent. The tensor function $\mathbf{f}_I(\varepsilon_{\mathrm{r}})$ is defined by (II.35). According to (32) $g_{\mathrm{m}I}$ can be considered as a function of ε_{r}, and hence

$$\left(\frac{\partial g_{\mathrm{m}I}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota} = \left(\frac{\partial g_{\mathrm{m}I}}{\partial \varepsilon_{\mathrm{r}}}\right)^*_{\vartheta_\iota}\left(\frac{\partial \varepsilon_{\mathrm{r}}}{\partial c_{02}}\right)^*_{n_{01},\, c_{03},\, \vartheta_\iota}, \tag{33}$$

where because of (32)

$$\frac{1}{RT}\left(\frac{\partial g_{\mathrm{m}I}}{\partial \varepsilon_{\mathrm{r}}}\right)_{\vartheta_\iota} = -\frac{1}{2kT}\,\tilde{\boldsymbol{\mu}}_{\mathrm{g}I}(1 - \mathbf{f}_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-2}\left(\frac{\partial \mathbf{f}_I}{\partial \varepsilon_{\mathrm{r}}}\right)_{\vartheta_\iota}\boldsymbol{\mu}_{\mathrm{g}I} \tag{34}$$

and because of Eq. (II.35)

$$\left(\frac{\partial f_{I\lambda}}{\partial \varepsilon_{\mathrm{r}}}\right)_{\vartheta_\iota} = \frac{f_{I\lambda}}{(\varepsilon_{\mathrm{r}} - 1)[\varepsilon_{\mathrm{r}} - \varkappa_{I\lambda}(\varepsilon_{\mathrm{r}} - 1)]}, \quad \lambda = x, y, z. \tag{35}$$

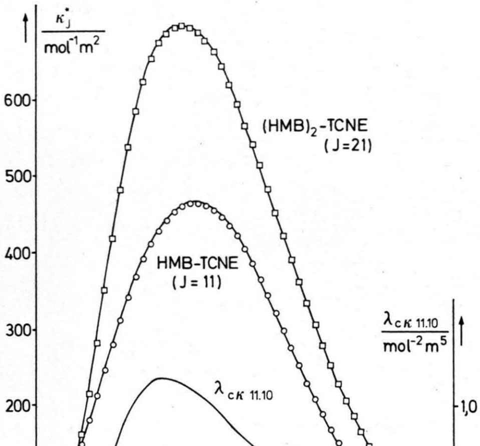

Fig. 1. Molar absorption coefficients $\varkappa_{11}^*$ and $\varkappa_{21}^*$ of the complexes HMB-TCNE and $(HMB)_2$-TCNE in CCl_4 at 298.15 K and coefficients $\lambda_{c\varkappa 11.10}$, estimated from the data, and $(\lambda_{c\varkappa 11.10})_{\mathrm{calc}}$, calculated according to (37). For $(\lambda_{c\varkappa 11.10})_{\mathrm{calc}}$ 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_2^*, v_3^* and v_{11}^* of the model molar volumes are estimated and it is shown that one has to assume $\lambda_{cvI.10} = 0$, $I = 2, 3, 11$. In Section 4.3 the quantities $\boldsymbol{\mu}_{gI}$, $\boldsymbol{\alpha}_{gI}$, $f_{I\lambda}$ and $\varkappa_{I\lambda}$ and the derivative $(\partial\varepsilon_\mathrm{r}/\partial c_{02})^*_{n_{01}}$ are estimated. With these data, listed in Tables 12 and 10, Eqs. (31) to (35) lead to

$$(\eta_{c11.10})_\mathrm{calc} = 1.28 \cdot 10^{-5}\ \mathrm{mol^{-1}\ m^3}\,.$$

The model molar absorption coefficient $\varkappa_{11}$ of HMB-TCNE depends on the relative permittivity ε_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]

$$\begin{aligned}\varkappa_I(\varepsilon_\mathrm{r}, n^2)/\tilde{\nu} = \tfrac{1}{3} S\, s_I(\tilde{\nu}(\varepsilon_\mathrm{r}^*, n^{*2}) \\ - \Delta\tilde{\nu}_I(\varepsilon_\mathrm{r}, n^2;\ \varepsilon_\mathrm{r}^*, n^{*2})) \\ \cdot \| \boldsymbol{\mu}_{\mathrm{ga}I}(\varepsilon_\mathrm{r}^*, n^{*2}) - \boldsymbol{\alpha}_{\mathrm{ga}I}[\boldsymbol{E}_{\mathrm{RM}I}(\varepsilon_\mathrm{r}, n^2) \\ - \boldsymbol{E}_{\mathrm{RM}I}(\varepsilon_\mathrm{r}^*, n^{*2})] \|^2 ,\end{aligned} \tag{36}$$

where

$$\begin{aligned}S &= 2\pi^2 N_\mathrm{A} \log e/h\,c\,\varepsilon_0 \\ &= 2.93512 \cdot 10^{60}\ \mathrm{C^{-2}\ mol^{-1}}\,,\end{aligned}$$

$s_I(\tilde{\nu}(\varepsilon_\mathrm{r}, n^2))$ is the bandshape function of the considered electronic absorption band, $\Delta\tilde{\nu}_I$ 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 ε_r^* to ε_r and from n^{*2} to n^2, $\boldsymbol{\mu}_{\mathrm{ga}I}(\varepsilon_\mathrm{r}, n^2)$ is the electric transition dipole moment and $\boldsymbol{\alpha}_{\mathrm{ga}I}$ the transition polarizability of the electronic band and $\boldsymbol{E}_{\mathrm{RM}I}(\varepsilon_\mathrm{r}, n^2)$ the effective electric field in a solution with given values of ε_r and n^2. Corresponding to (14) and (36) the coefficient $\lambda_{c\varkappa 11.10}(\tilde{\nu})$ can be represented as

$$\begin{aligned}\lambda_{c\varkappa 11.10}(\tilde{\nu}) &= \left(\frac{\partial\varkappa_{11}(\tilde{\nu})}{\partial c_{02}}\right)^*_{n_{01},\,c_{03},\,\vartheta_\iota} \\ &= \left(\frac{\partial\varkappa_{11}(\tilde{\nu})}{\partial\varepsilon_\mathrm{r}}\right)^*_{\vartheta_\iota} \left(\frac{\partial\varepsilon_\mathrm{r}}{\partial c_{02}}\right)^*_{n_{01},\,c_{03},\,\vartheta_\iota} \\ &\quad + \left(\frac{\partial\varkappa_{11}(\tilde{\nu})}{\partial n^2}\right)^*_{\vartheta_\iota} \left(\frac{\partial n^2}{\partial c_{02}}\right)^*_{n_{01},\,c_{03},\,\vartheta_\iota} .\end{aligned} \tag{37}$$

Neglecting the change of polarizability during the absorption process, i.e. assuming $\boldsymbol{\alpha}_{\mathrm{a}I} = \boldsymbol{\alpha}_{\mathrm{g}I}$, from (23) [54] follows for the shift

$$\begin{aligned}h\,c\,\Delta\tilde{\nu}_I(\varepsilon_\mathrm{r}, n^2; 1{,}1) &= h\,c\,(\tilde{\nu} - \tilde{\nu}_0) \\ &= -\tfrac{1}{2}(\tilde{\boldsymbol{\mu}}_{\mathrm{a}I} - \tilde{\boldsymbol{\mu}}_{\mathrm{g}I})(\mathbf{1} - \mathbf{f}'_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-1}\,\mathbf{f}'_I(\boldsymbol{\mu}_{\mathrm{a}I} - \boldsymbol{\mu}_{\mathrm{g}I}) \\ &\quad - (\tilde{\boldsymbol{\mu}}_{\mathrm{a}I} - \tilde{\boldsymbol{\mu}}_{\mathrm{g}I})(\mathbf{1} - \mathbf{f}_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-1}\,\mathbf{f}_I\,\boldsymbol{\mu}_{\mathrm{g}I}\,,\end{aligned} \tag{38}$$

where $\mathbf{f}_I(\varepsilon_\mathrm{r})$ is defined by (II.35) and (II.36) and $\mathbf{f}'_I = \mathbf{f}_I(n^2)$. $\boldsymbol{\mu}_{\mathrm{a}I}$ is the electric dipole moment of the molecule A_I in the considered excited electronic state. According to (22) [55] it is again with $\boldsymbol{\alpha}_{\mathrm{a}I} = \boldsymbol{\alpha}_{\mathrm{g}I}$

$$\begin{aligned}\boldsymbol{E}_{\mathrm{RM}I} &= (\mathbf{1} - \mathbf{f}_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-1}\,\mathbf{f}_I\,\boldsymbol{\mu}_{\mathrm{g}I} \\ &\quad + \tfrac{1}{2}(\mathbf{1} - \mathbf{f}'_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-1}\,\mathbf{f}'_I(\boldsymbol{\mu}_{\mathrm{a}I} - \boldsymbol{\mu}_{\mathrm{g}I})\,.\end{aligned} \tag{39}$$

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 $A_1 \rightarrow A_1$ type, i.e. the dipole moments $\boldsymbol{\mu}_{\mathrm{g}11}$ and $\boldsymbol{\mu}_{\mathrm{a}11}$ and the transition dipole moment $\boldsymbol{\mu}_{\mathrm{ga}11}$ 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)

$$\begin{aligned}\left(\frac{\partial\varkappa_I}{\partial\varepsilon_\mathrm{r}}\right)^*_{\vartheta_\iota} &= \tilde{\nu}\left(\frac{\partial(\varkappa_I/\tilde{\nu})}{\partial\varepsilon_\mathrm{r}}\right)^*_{\vartheta_\iota} \\ &= \varkappa_I^*\left[\frac{2}{\|\boldsymbol{\mu}^*_{\mathrm{ga}I}\|^2}\,\tilde{\boldsymbol{\mu}}^*_{\mathrm{ga}I\mathrm{z}}\,\boldsymbol{\alpha}_{\mathrm{ag}I\mathrm{zz}}\left(\frac{\partial\boldsymbol{E}_{\mathrm{RM}I\mathrm{z}}}{\partial\varepsilon_\mathrm{r}}\right)^*_{\vartheta_\iota}\right. \\ &\quad \left. - \left(\frac{\partial\ln(\varkappa(\tilde{\nu}')/\tilde{\nu}')}{\partial\tilde{\nu}'}\right)^*_{\tilde{\nu}'=\tilde{\nu}}\left(\frac{\partial\Delta\tilde{\nu}_I}{\partial\varepsilon_\mathrm{r}}\right)^*_{\vartheta_\iota}\right]\end{aligned} \tag{40}$$

and a similar equation for $(\partial\varkappa_I/\partial n^2)^*_{\vartheta_\iota}$, where ε_r has to be replaced by n^2 in (40). From (38) follows

$$\begin{aligned}h\,c\left(\frac{\partial\Delta\tilde{\nu}_I}{\partial\varepsilon_\mathrm{r}}\right)_{\vartheta_\iota} &= -(\tilde{\boldsymbol{\mu}}_\mathrm{a} - \tilde{\boldsymbol{\mu}}_\mathrm{g})(\mathbf{1} - \mathbf{f}_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-2} \\ &\quad \cdot\left(\frac{\partial\mathbf{f}_I}{\partial\varepsilon_\mathrm{r}}\right)_{\vartheta_\iota}\boldsymbol{\mu}_{\mathrm{g}I}\,,\end{aligned} \tag{41}$$

$$\begin{aligned}h\,c\left(\frac{\partial\Delta\tilde{\nu}_I}{\partial n^2}\right)_{\vartheta_\iota} &= -\tfrac{1}{2}(\tilde{\boldsymbol{\mu}}_{\mathrm{a}I} - \tilde{\boldsymbol{\mu}}_{\mathrm{g}I})(\mathbf{1} - \mathbf{f}'_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-2} \\ &\quad \cdot\left(\frac{\partial\mathbf{f}'_I}{\partial n^2}\right)_{\vartheta_\iota}(\boldsymbol{\mu}_{\mathrm{a}I} - \boldsymbol{\mu}_{\mathrm{g}I})\,,\end{aligned} \tag{42}$$

and from Eq. (39)

$$\left(\frac{\partial\boldsymbol{E}_{\mathrm{RM}I}}{\partial\varepsilon_\mathrm{r}}\right)_{\vartheta_\iota} = (\mathbf{1} - \mathbf{f}_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-2}\left(\frac{\partial\mathbf{f}_I}{\partial\varepsilon_\mathrm{r}}\right)_{\vartheta_\iota}\boldsymbol{\mu}_{\mathrm{g}I}\,, \tag{43}$$

$$\begin{aligned}\left(\frac{\partial\boldsymbol{E}_{\mathrm{RM}I}}{\partial n^2}\right)_{\vartheta_\iota} &= \tfrac{1}{2}(\mathbf{1} - \mathbf{f}'_I\,\boldsymbol{\alpha}_{\mathrm{g}I})^{-2} \\ &\quad \cdot\left(\frac{\partial\mathbf{f}'_I}{\partial n^2}\right)_{\vartheta_\iota}(\boldsymbol{\mu}_{\mathrm{a}I} - \boldsymbol{\mu}_{\mathrm{g}I})\,.\end{aligned} \tag{44}$$

The derivative $(\partial\mathbf{f}_I/\partial\varepsilon_\mathrm{r})_{\vartheta_\iota}$ is given by (35); for the derivative $(\partial\mathbf{f}'_I/\partial n^2)_{\vartheta_\iota}$ a similar equation holds true, where ε_r has to be replaced by n^2.

In this section, the magnitude $\| \boldsymbol{\mu}_{\text{ga11}} \|$ of the transition dipole moment will be estimated, and in Sect. 4.4, the values of $\mu_{\text{a11}z}$ and $(\alpha_{\text{ga}I})_{zz}$. The derivatives $(\partial \ln (\varkappa_{11}(\tilde{\nu}')/\tilde{\nu}')/\partial \tilde{\nu}')^*_{\tilde{\nu}'=\tilde{\nu}}$, which are also needed for the evaluation of electro-optical absorption measurements in Sect. 4.4, can be obtained from the estimated values of $\varkappa^*_{11}$ as shown in Figure 1. With these data, listed in Tables 12 and 14, Eqs. (37) and (41) to (44) lead to the values $(\lambda_{c\varkappa 11.10})_{\text{calc}}$ as represented in Figure 1.

The value $(\eta_{c11.10})_{\text{calc}}$ 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 $(\lambda_{c\varkappa 11.10})_{\text{calc}}$ calculated from (37) are less than 0.1% of the values of $\lambda_{c\varkappa 11.10}$ estimated assuming model II. Hence comparison of calculated and estimated coefficients $\eta_{c11.10}$ and $\lambda_{c\varkappa 11.10}$ disclose that only model I agrees with the observed data. For estimations based on model I the coefficients are negligibly small compared to K^*_{c21} and $\varkappa^*_{21}$, 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 of the absorption band also into account.

From the estimated values of $\varkappa^*_{11}$ and $\varkappa^*_{21}$, Fig. 1, the magnitudes $\| \boldsymbol{\mu}^*_{\text{ga11}} \|$ and $\| \boldsymbol{\mu}^*_{\text{ga21}} \|$ of the electric transition dipole moments of the solute molecules may be obtained, for example by using Eq. (6) of the previous paper [57]. With the electric dipole moments and the transition polarizabilities, as estimated in Sects. 4.3 and 4.4, the magnitudes $\| (\boldsymbol{\mu}_{\text{ga11}})_{0\text{e}} \|$ and $\| (\boldsymbol{\mu}_{\text{ga21}})_{0\text{e}} \|$ of the permanent transition dipole moments of the isolated molecules may be calculated according to (66) [57]. The results are listed in Table 12.

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 $\varkappa^*_{11}$ and $\varkappa^*_{21}$ and negligible contributions due to $\lambda_{c\varkappa 11.10}$ and $\eta_{c11.10}$. The data confirm the assumptions, i.e. the quantities $B_{c\mathbf{K}1}/A_{c1}$ and $B_{c\mathbf{K}2}/A_{c2}$ depend on $\tilde{\nu}$ 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 $K^*_{c11}(T)$ and $K^*_{c21}(T)$ the model standard reaction enthalpies $\Delta_R h^*_c$, the model standard reaction entropies $\Delta_R s^*_c$ and the model standard reaction Gibbs energies $\Delta_R g^*_c$ can be estimated using (IV.35), (IV.39), and (IV.41). The values are listed in Table 7.

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

T	$K^*_{c11}/10^{-4}$	$K^*_{c21}/10^{-6}$
283.15	3032 ± 85	4300 ± 340
293.15	1901 ± 46	1424 ± 62
298.15	1510 ± 3	734 ± 7
303.15	1198 ± 22	506 ± 19

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

R	HMB-TCNE (11)	(HMB)$_2$-TCNE (21)
$\Delta_R g^*_c$/J mol^{-1}	4685.9 ± 0.5	17890 ± 25
$\Delta_R h^*_c/10^3$ J mol^{-1}	−32.9 ± 1.9	−78 ± 16
$\Delta_R s^*_c$/J mol^{-1} K^{-1}	−126.0 ± 6.4	−322 ± 54

The values of the maximal absorption coefficient

$$(\varkappa^*_{11})_{\text{max}} = 466 \text{ m}^2 \text{ mol}^{-1} \quad \text{at}$$

$$(\tilde{\nu}_{11})_{\text{max}} = 1.87 \cdot 10^6 \text{ m}^{-1} \quad \text{and of}$$

$$\Delta_{11} h^*_c = -32.9 \cdot 10^3 \text{ J mol}^{-1}$$

obtained in our studies for the complex HMB-TCNE are in excellent agreement with the data obtained by Briegleb, Czekalla and Reuss [16]

$$\varkappa_{\text{max}} = 478 \text{ m}^2 \text{ mol}^{-1}, \quad \tilde{\nu}_{\text{max}} = 1.88 \cdot 10^6 \text{ m}^{-1}$$

and $\Delta_{11} h_c = -32.4 \cdot 10^3$ J mol^{-1} in spite of the fact that they considered only the formation of the 1:1 complex HMB-TCNE. The value of $K^*_{c11} = 0.148$ 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], $K^*_{c11} = 0.123$ (at 298 K) and $\varkappa_{\text{max}} = 514$ m^2 mol^{-1} and by Liao and Chan [58] $K^*_{c11} = 0.099$ (at 298 K) and $\Delta_{11} h^*_c = -27 \cdot 10^3$ J mol^{-1}, where only the 1:1 complex formation was taken into account, show also some deviations from our results. The values of $K^*_{c11} = 0.180$ and $K^*_{c21} = 1.10 \cdot 10^{-3}$ at 293 K obtained by Foster and Kulevsky [17] are 5% and 23% lower than our values. Further data reported 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 $\Delta_{11}h_c^* = -31.27 \cdot 10^3\ \mathrm{J\,mol^{-1}}$ in CH_2Cl_2 obtained by Herndon, Feuer and Mitchell [9] agrees well with our value, also because they investigated only the interval $c_{02} = 20$ to $100\ \mathrm{mol\,m^{-3}}$, where the formation of the 2:1 complex is rather small.

4.2. *Density Measurements*

The densities ϱ were measured of 23 sets of solutions in CCl_4 at 298.15 K with fixed values of the mass fraction w_{02}^+ of HMB, each set consisting of a few solutions with variable values of the mass fraction w_{03} of TCNE ($c_{02}^+ = 32$ to $510\ \mathrm{mol\,m^{-3}}$, $c_{03} = 5$ to $28\ \mathrm{mol\,m^{-3}}$). Analysis of the variance (F- and t-test) of the data has shown that in the investigated concentration intervals the inverse density ϱ^{-1} is linearly dependent on the mass fraction w_{03}. Hence (1) is simplified to

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

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

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

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

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

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

agree excellently with those of Le Fèvre [59].

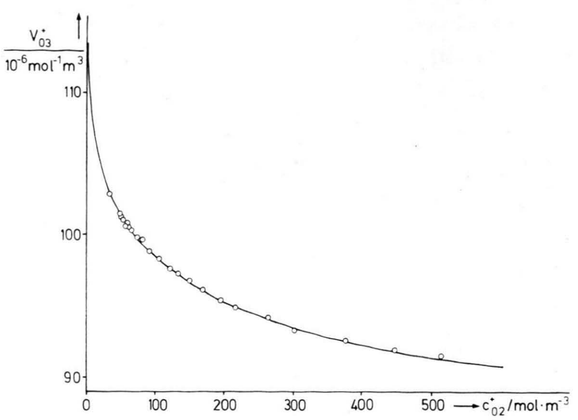

Fig. 2. Values of the limit V_{03}^+ of the partial molar volumes of TCNE for solutions of HMB and TCNE in CCl_4 at 298.15 K. The curve is calculated according to (19) using the data in Tables 2 and 8.

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_{V0}, B_{cV1}, B_{cV2}, … . 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 $\lambda_{cvJ.\alpha_1\alpha_2}$, $J = 1, 2, 3$, 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 $\eta_{c11.10} = 0$, $\lambda_{cv11.10} = 0$ — the equations are simplified to

$$B_{V0} = V_{03}^*\,,$$
$$B_{cV1} = A_{c1}(v_{11}^* - v_2^*)\,,$$
$$B_{cV2} = A_{c2}(v_{21}^* - 2\,v_2^*)\,,$$

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.

Number of coefficients assumed unequal zero	2	3	4
$B_{V0}/10^{-5}\ \mathrm{m^3\,mol^{-1}}$	−46.5	11.33 ± 0.32	11.01
$t(B_{V0})$	6.4	71.8	44.8
$B_{cV1}/10^{-7}\ \mathrm{m^6\,mol^{-2}}$	305.3	156.03 ± 0.71	157.08
$t(B_{cV1})$	26.0	442.6	216.6
$B_{cV2}/10^{-9}\ \mathrm{m^9\,mol^{-3}}$	—	63.41 ± 0.27	62.56
$t(B_{cV2})$	—	477.7	118.1
$B_{cV3}/10^{-11}\ \mathrm{m^{12}\,mol^{-4}}$	—	—	0.153
$t(B_{cV3})$	—	—	1.6
F	—	230000	2.7

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 $c_{02} \to 0$ and $c_{03} \to 0$. With the above data the following values are estimated

$$V_{01}^{*} = (97.067 \pm 0.001) \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}},$$
$$V_{02}^{*} = v_{2}^{*} = (175.31 \pm 0.07) \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}},$$
$$V_{03}^{*} = v_{3}^{*} = (113.3 \pm 3.2) \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}},$$
$$v_{11}^{*} = (278.65 \pm 0.52) \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}},$$
$$v_{21}^{*} = (437.07 \pm 0.92) \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}}.$$

Assuming model II — the formation of only the 1:1 complex and $\eta_{c11.10} \neq 0$ — leads to a modification of the equation for B_{cV2}

$$B_{cV2} = A_{c2} v_{3}^{*} + A_{c1} \cdot [(c^{\ominus})^{-1} \eta_{c11.10} (v_{11}^{*} - v_{2}^{*}) + \lambda_{cv11.10}].$$

From the data follows

$$\lambda_{cv11.10} = -8.76 \cdot 10^{-8}\,\mathrm{m^6\,mol^{-2}}.$$

The results can be explained quite naturally with model I. There is a decrease of the molar volumes

$$\Delta_{11} v^{*} = -9.96 \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}} \quad \text{and}$$
$$\Delta_{21} v^{*} = -26.85 \cdot 10^{-6}\,\mathrm{m^3\,mol^{-1}}$$

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 $\lambda_{cv11.10}$, namely a decrease of approximately 15% in the investigated concentration interval ($c_{02} = 0$ to 500 mol^{-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 ε_r and the refractive indices n at the wavenumber $\tilde{\nu} = 9.259 \cdot 10^5\,\mathrm{m^{-1}}$ 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 m^{-3}, $c_{03} = 0$ to 41 mol m^{-3}). Analysis of variance (F- and t-test) of the data has shown that in the investigated concentration intervals the specific electric susceptibility $(\varepsilon_r - 1)/\varrho$ is linearly dependent on the mass fraction w_{03}. Hence (1) is simplified to

$$\mathsf{P}_{w\mathsf{Z}} = \frac{\varepsilon_r - 1}{\varrho} = \frac{\varepsilon_r^{+} - 1}{\varrho^{+}} + \left(\frac{\mathsf{Z}_{03}^{+}}{M_3} - \frac{\varepsilon_r^{+} - 1}{\varrho^{+}}\right) w_{03}, \tag{47}$$

where ε_r^{+} and Z_{03}^{+} are the limits of the relative permittivity ε_r and of the partial molar electric susceptibility Z_{03} of TCNE for $w_{03} \to 0$, respectively. Linear regression according to (47) leads to values for $(\varepsilon_r^{+} - 1)/\varrho^{+}$ and $\mathsf{Z}_{03}^{+}(w_{02}^{+})$.

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

$$\frac{\varepsilon_r^{+} - 1}{\varrho^{+}} = \frac{\varepsilon_r^{*} - 1}{\varrho^{*}} + \left[\frac{\mathsf{Z}_{02}^{*}}{M_2} - \frac{\varepsilon_r^{*} - 1}{\varrho^{*}}\right] w_{02}^{+}, \tag{48}$$

where ε_r^{*} and Z_{02}^{*} are the limits of the permittivity (permittivity of the pure solvent CCl_4) and of the partial molar electric susceptibility Z_{02} of HMB for $w_{02}^{+} \to 0$, respectively. Linear regression according to (48) leads to values for $(\varepsilon_r^{*} - 1)/\varrho^{*}$ and Z_{02}^{*}.

Equations similar to (47) and (48) but with ε_r substituted by n^2 hold for $\mathsf{P}_{w\mathsf{Z}'} = (n^2 - 1)/\varrho$. The evaluation of data leads to $(n^{*2} - 1)/\varrho^{*}$, $\mathsf{Z}_{02}^{\prime *}$ and $\mathsf{Z}_{03}^{\prime +}(w_{02}^{+})$.

With the value of ϱ^{*}, 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_{02}^{*} and $\mathsf{Z}_{02}^{\prime *}$ obtained are listed in Table 12, the values of Z_{03}^{+} and $\mathsf{Z}_{03}^{\prime +}$ 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 $B_{\mathsf{Z}0}$, $B_{c\mathsf{Z}1}$, $B_{c\mathsf{Z}2}$, $B_{\mathsf{Z}'0}$, $B_{c\mathsf{Z}'1}$ and $B_{c\mathsf{Z}'2}$ as given in column "3" of Table 9.

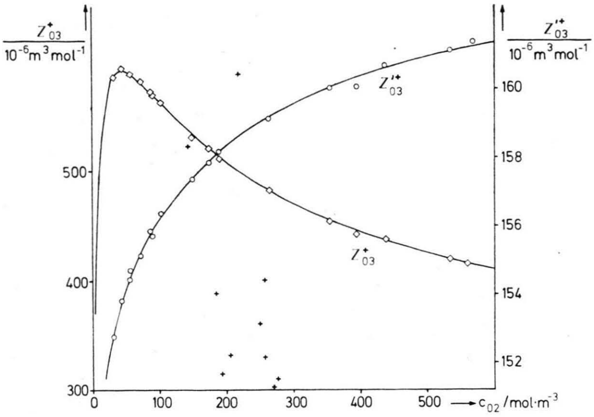

Fig. 3. Values of the limits $\mathbf{Z}^+_{03}$ and $\mathbf{Z}'^+_{03}$ of partial molar electric susceptibility and refraction of TCNE for solutions of HMB and TCNE in CCl_4 at 298.15 K. The curves are calculated using (19) and the data in Tables 2 and 9. The crosses (+) represent values of $\mathbf{Z}^+_{03}$ according to the data of Briegleb, Czekalla, and Reuss [16]; for these values the scale factor on the left-hand side of the figure has to be multiplied by 2.

The limit $\mathbf{Z}^*_{02}$ of the partial molar electric susceptibility is related to the limit ζ^*_2 of the model molar electric susceptibility of HMB according to (I.78) and (I.83) by

$$\zeta^*_J = \mathbf{Z}^*_{0J} - \lambda_{c\zeta 1.10}/V^*_{01}\,. \tag{49}$$

A similar equation holds for ζ'^*_J, where $\mathbf{Z}^*_{0J}$ is to be substituted by $\mathbf{Z}'^*_{0J}$ and $\lambda_{c\zeta 1.10}$ by $\lambda_{c\zeta' 1.10}$. Similarly for the further evaluation of the quantities $B_{\mathbf{Z}0}, \ldots, B_{c\mathbf{Z}'2}$ according to (22) to (24) some of the coefficients $\lambda_{c\zeta J.\alpha_1\alpha_2}$ and $\lambda_{c\zeta' J.\alpha_1\alpha_2}$ are needed, which are defined by (14).

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 CCl_4 at 298.15 K.

Number of coefficients assumed unequal zero	2	3	4
$B_{\mathbf{Z}0}/10^{-5}$ m^3 mol^{-1}	−215	16.5 ± 4.8	13.6
$t(B_{\mathbf{Z}0})$	5.6	7.0	3.8
$B_{c\mathbf{Z}1}/10^{-7}$ m^6 mol^{-2}	1677	1081 ± 10	1091
$t(B_{c\mathbf{Z}1})$	27.2	210.9	103.1
$B_{c\mathbf{Z}2}/10^{-9}$ m^9 mol^{-3}		224.8 ± 3.4	217.3
$t(B_{c\mathbf{Z}2})$	—	134.6	29.3
$B_{c\mathbf{Z}3}/10^{-11}$ m^{12} mol^{-4}	—	—	1.23
$t(B_{c\mathbf{Z}3})$	—	—	1.0
F	—	18000	1.1
$B_{\mathbf{Z}'0}/10^{-5}$ m^3 mol^{-1}	−110	14.30 ± 0.34	13.96
$t(B_{\mathbf{Z}'0})$	5.3	85.8	56.9
$B_{c\mathbf{Z}'1}/10^{-7}$ m^6 mol^{-2}	550	231.17 ± 0.74	232.31
$t(B_{c\mathbf{Z}'1})$	16.7	639.7	322.0
$B_{c\mathbf{Z}'2}/10^{-9}$ m^9 mol^{-3}	—	120.64 ± 0.24	119.57
$t(B_{c\mathbf{Z}'2})$	—	1022.9	236.7
$B_{c\mathbf{Z}'3}/10^{-11}$ m^3 mol^{-1}	—	—	1.44
$t(B_{c\mathbf{Z}'3})$	—	—	1.8
F	—	1000000	3.2

The further evaluation of the quantities ζ^*_J and ζ'^*_J, which may lead to the permanent electric dipole moment $\boldsymbol{\mu}_{gJ}$ or the static polarizability $\boldsymbol{\alpha}_{gJ}$ and the polarizability $\mathbf{A}_{gJ}$ at the wavenumber $\tilde{\nu}$ used for the investigation ($\tilde{\nu} = 9.259 \cdot 10^5$ m^{-1}) of the molecule A_J 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 ζ^*_J and ζ'^*_J, as represented by (II.41) and (II.51), are dependent on ε_r and n^2, respectively, at least at fixed values of the temperature T and the pressure p. Hence

$$\lambda_{c\zeta I.10} = \left(\frac{\partial \zeta_I}{\partial c_{02}}\right)^*_{c_{03},\,\vartheta_\iota} = \left(\frac{\partial \zeta_I}{\partial \varepsilon_r}\right)^*_{\vartheta_\iota} \left(\frac{\partial \varepsilon_r}{\partial c_{02}}\right)^*_{c_{03},\,\vartheta_\iota}, \tag{50}$$

and

$$\begin{aligned}\lambda_{c\zeta I.20} &= \frac{1}{2}\left(\frac{\partial^2 \zeta_I}{\partial c^2_{02}}\right)^*_{c_{03},\,\vartheta_\iota} \\ &= \frac{1}{2}\left[\left(\frac{\partial \zeta_I}{\partial \varepsilon_r}\right)^*_{\vartheta_\iota}\left(\frac{\partial^2 \varepsilon_r}{\partial c^2_{02}}\right)^*_{c_{03},\,\vartheta_\iota} + \left(\frac{\partial^2 \zeta_I}{\partial \varepsilon^2_r}\right)^*_{\vartheta_\iota}\left(\frac{\partial \varepsilon_r}{\partial c_{02}}\right)^{*2}_{c_{03},\,\vartheta_\iota}\right].\end{aligned} \tag{51}$$

Similar equations hold true for $\lambda_{c\zeta I.01}$ and $\lambda_{c\zeta I.02}$, where the indices "2" and "3" have to be exchanged. The coefficients $\lambda_{c\zeta I.11}$ and $\lambda_{c\zeta I.21}$ can similarly be expressed. Representations for $\lambda_{c\zeta' I.\alpha_1\alpha_2}$ result from similar equations, where ε_r is substituted by n^2.

The derivatives $(\partial\varepsilon_r/\partial c_{02})_{c_{03},\,\vartheta_\iota}$, $(\partial\varepsilon_r/\partial c_{03})_{c_{02},\,\vartheta_\iota}, \ldots$ follow from (47), (48), (45) and (46), for example,

$$\left(\frac{\partial \varepsilon_r}{\partial c_{0J}}\right)^*_{c_{0J'}} = \mathbf{Z}^*_{0J} - (\varepsilon^*_r - 1)\, V^*_{0J}\,. \tag{52}$$

Similar equations hold for

$$(\partial n^2/\partial c_{02})^*_{c_{03},\,\vartheta_\iota},\ (\partial n^2/\partial c_{03})^*_{c_{02},\,\vartheta_\iota}, \ldots,$$

where $\mathbf{Z}^*_{0J}$ and ε^*_r have to be substituted by $\mathbf{Z}'^*_{0J}$ 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 $(\partial\zeta_I/\partial\varepsilon_r)^*_{\vartheta_\iota}$, $(\partial^2\zeta_I/\partial\varepsilon^2_r)_{\vartheta_\iota}, \ldots$ follow from (II.41), and an example is given by (II.42). Similarly the derivatives $(\partial\zeta_I/\partial n^2)^*_{\vartheta_\iota}, \ldots$ 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 ε_r and n^2 with respect to c_{02} and c_{03} for solutions of HMB and TCNE in CCl_4 at 298.15 K.

y	ε_r	n^2
$(\partial y/\partial c_{02})^*/10^{-6}\,m^3\,mol^{-1}$	32.17 ± 0.21	38.531 ± 0.068
$(\partial y/\partial c_{03})^*/10^{-6}\,m^3\,mol^{-1}$	26 ± 48	17.9 ± 4.9
$(\partial^2 y/\partial c_{02}^2)^*/10^{-6}\,m^6\,mol^{-2}$	0	0
$(\partial^2 y/\partial c_{02}\,\partial c_{03})^*/10^{-6}\,m^6 \cdot mol^{-2}$	85.0 ± 7.3	31.9 ± 7.9
$(\partial^3 y/\partial c_{02}^2\,\partial c_{03})^*/10^{-6}\,m^9 \cdot mol^{-3}$	-25.4 ± 2.2	-0.89 ± 0.23

abilities of CCl_4 must be known. The values

$$a_{w1}^3 = 38.68 \cdot 10^{-30}\,m^3 \quad \text{and}$$

$$\mathrm{tr}\,(\boldsymbol{\alpha}_{g1})/3 = 12.46 \cdot 10^{-40}\,CV^{-1}\,m^2$$

have been determined previously [37]. With the above value of n^{*2} and (II.51) follows

$$\mathrm{tr}\,(\mathbf{A}_{g1})/3 = 11.57 \cdot 10^{-40}\,CV^{-1}\,m^2 .$$

The values $\lambda_{c\zeta 1.10}$ and $\lambda_{c\zeta' 1.10}$ obtained from (50) are listed in Table 11. With these data and Z_{02}^* or $\mathsf{Z}_{02}'^*$ the values of ζ_2^* or $\zeta_2'^*$ result according to (49); they are reported in Table 12. The details of the further evaluation of ζ_2^* and $\zeta_2'^*$ leading to the polarizabilities $\boldsymbol{\alpha}_{g2}$ and $\mathbf{A}_{g2}$ 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 $B_{\mathsf{Z}0}$ and $B_{\mathsf{Z}'0}$, Table 9, can be evaluated. According to (22) these data lead to ζ_3^* and $\zeta_3'^*$ and as above to $\boldsymbol{\alpha}_{g3}$ and $\mathbf{A}_{g3}$ of TCNE; the data necessary and the results are listed in Table 12.

With the values obtained for HMB and TCNE the derivatives $(\partial\zeta_I/\partial\varepsilon_r)^*$, $(\partial\zeta_I'/\partial n^2)$, ... can be calculated for $I = 2$ and 3 using (II.41) and (II.51). These quantities together with the derivatives $(\partial\varepsilon_r/\partial c_{02})$, ... as given in Table 10 allow the calculation of $\lambda_{c\zeta I.\alpha_1\alpha_2}$, $I = 2, 3$, using (50) or (51) and similar equations; the results are listed in Table 11. With these coefficients and the values of $B_{c\mathsf{Z}1}$, $B_{c\mathsf{Z}'1}$, Table 9, and A_{c1}, the model molar electric susceptibilities ζ_{11}^* and $\zeta_{11}'^*$ of the complex HMB-TCNE can be obtained; the values are listed in Table 12.

For the estimation of the interaction distances $(a_{I\lambda})_s$, $I = 11$, $\lambda = x, y, z$, 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 $(\mathbf{A}_{g11})_b = (\mathbf{A}_{g2})_{0e} + (\mathbf{A}_{g3})_{0e}$ assuming the described configuration. Similarly the static polarizability was estimated as

$$(\boldsymbol{\alpha}_{g11})_s = (\boldsymbol{\alpha}_{g2})_{0e} + (\boldsymbol{\alpha}_{g3})_{0e} .$$

With these data the evaluation of ζ_{11}^* and $\zeta_{11}'^*$ was done as described previously [37]. The data used and the obtained values of $(\boldsymbol{\mu}_{g11})_{0e}$ and $(\boldsymbol{\alpha}_{g11})_{0e}$ are listed in Table 12.

Assuming model I — the formation of the 1:1 and the 2:1 complex — from the quantities $B_{c\mathsf{Z}2}$ and $B_{c\mathsf{Z}'2}$, Table 9, A_{c1} and A_{c2} the model molar electric susceptibilities ζ_{21}^* and $\zeta_{21}'^*$ of the complex $(HMB)_2$-TCNE can be obtained, if the values of the coefficients $\lambda_{c\zeta J.\alpha_1\alpha_2}$ and $\lambda_{c\zeta' J.\alpha_1\alpha_2}$, $J = 1, 2, 3$ and 11, as given in Table 11 are used. The coefficients with $J = 1, 2$ and 3 have been discussed above. The coefficients $\lambda_{c\zeta 11.10}$ and $\lambda_{c\zeta' 11.10}$ 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 ζ_{21}^* and $\zeta_{21}'^*$ are listed in

$(J.\,\alpha_1\,\alpha_2)$	$\lambda_{c\zeta J.\alpha_1\alpha_2}$	$\lambda_{c\zeta' J.\alpha_1\alpha_2}$	unit
(1.10)	$(572.9 \pm 3.7) \cdot 10^{-12}$	$(653.1 \pm 1.2) \cdot 10^{-12}$	$m^6\,mol^{-2}$
(1.01)	$(4.6 \pm 8.5) \cdot 10^{-10}$	$(3.03 \pm 0.83) \cdot 10^{-10}$	$m^6\,mol^{-2}$
(3.10)	$(8.4 \pm 4.8) \cdot 10^{-10}$	$(9.05 \pm 0.77) \cdot 10^{-10}$	$m^6\,mol^{-2}$
(1.11)	$(15.1 \pm 1.3) \cdot 10^{-10}$	$(0.54 \pm 0.13) \cdot 10^{-10}$	$m^9\,mol^{-3}$
(1.20)	$-(55.2 \pm 0.72) \cdot 10^{-16}$	$-(79.81 \pm 0.28) \cdot 10^{-16}$	$m^9\,mol^{-3}$
(1.21)	$-(226 \pm 20) \cdot 10^{-12}$	$-(7.5 \pm 1.9) \cdot 10^{-12}$	$m^{12}\,mol^{-4}$
(2.10)	$(11.65 \pm 0.49) \cdot 10^{-10}$	$(13.91 \pm 0.54) \cdot 10^{-10}$	$m^6\,mol^{-2}$
(2.01)	$(9 \pm 17) \cdot 10^{-10}$	$(6.5 \pm 1.8) \cdot 10^{-10}$	$m^6\,mol^{-2}$
(2.11)	$(30.8 \pm 2.9) \cdot 10^{-10}$	$(1.17 \pm 0.28) \cdot 10^{-10}$	$m^9\,mol^{-3}$
(3.20)	$-(75 \pm 29) \cdot 10^{-16}$	$-(104.7 \pm 6.2) \cdot 10^{-16}$	$m^9\,mol^{-3}$
(11.10)	$(61.2 \pm 1.3) \cdot 10^{-10}$	$(24.0 \pm 1.0) \cdot 10^{-10}$	$m^6\,mol^{-2}$

Table 11. Estimated values of coefficients $\lambda_{c\zeta J.\alpha_1\alpha_2}$ and $\lambda_{c\zeta' J.\alpha_1\alpha_2}$ needed for the evaluation of refractometric and permittivity measurements.

Table 12. Determination of electric dipole moments and polarizabilities from measurements of solutions of HMB and TCNE in CCl_4 at 298.15 K.

J	HMB 2	TCNE 3	HMB-TCNE 11	$(HMB)_2$-TCNE 21
$M_J/\text{kg mol}^{-1}$	0.162274	0.128093	0.290367	0.452641
$w_{0J}/10^{-4}$	$24-580$	$4-35$	—	—
V^*_{0J} (or v^*_J)$/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	175.31 ± 0.07	113.3 ± 3.2	278.65 ± 0.52	437.07 ± 0.92
$\mathsf{Z}'^*_{0J}/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	232.13 ± 0.06	143.0 ± 3.4	—	—
$\mathsf{Z}^*_{0J}/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	247.45 ± 0.21	165 ± 48	—	—
$\zeta'^*_J/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	225.40 ± 0.06	139.9 ± 3.5	371.7 ± 1.3	602.7 ± 1.3
$\zeta^*_J/10^{-6}\,\text{m}^3\,\text{mol}^{-1}$	241.56 ± 0.22	160 ± 49	850 ± 14	721 ± 13
$[(a_{Jx})_\text{l}; (a_{Jy})_\text{l}; (a_{Jz})_\text{l}]/10^{-10}\,\text{m}$	4.9; 4.9; 2.0	3.8; 3.6; 1.8	4.9; 4.9; 3.6	4.9; 4.9; 5.4
$[(a_{Jx})_\text{s}; (a_{Jy})_\text{s}; (a_{Jz})_\text{s}]/10^{-10}\,\text{m}$	5.3; 5.3; 2.4	4.2; 4.0; 2.2	5.3; 5.3; 4.0	5.3; 5.3; 5.8
$(a_{Jx})_\text{s}(a_{Jy})_\text{s}(a_{Jz})_\text{s}/10^{-30}\,\text{m}^3$	67.42	36.96	112.4	162.9
$(a^3_{\text{w}J})_\text{0k}/10^{-30}\,\text{m}^3$	69.50	44.92	110.5	173.3
$(\varkappa_{Jx})_\text{s}; (\varkappa_{Jy})_\text{s}; (\varkappa_{Jz})_\text{s}$	0.223; 0.223; 0.555	0.239; 0.254; 0.507	0.295; 0.295; 0.411	0.345; 0.345; 0.310
$[(\mathbf{A}_{\text{g}Jx})_\text{b}; (\mathbf{A}_{\text{g}Jy})_\text{b}; (\mathbf{A}_{\text{g}Jz})_\text{b}]/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	31.55; 31.55; 19.25	19.66; 14.10; 8.30	48.65; 42.78; 25.79	76.56; 70.69; 42.82
$\text{tr}(\mathbf{A}_{\text{g}J})_\text{b}/3 \cdot 10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	27.45	14.02	39.07	63.36
$(\mathbf{A}_{\text{g}Jx})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	27.91 ± 0.01	20.74 ± 0.52	48.86 ± 0.17	74.30 ± 0.16
$(\mathbf{A}_{\text{g}Jy})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	27.91 ± 0.01	14.87 ± 0.37	42.97 ± 0.15	68.60 ± 0.15
$(\mathbf{A}_{\text{g}Jz})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	17.03 ± 0.01	8.76 ± 0.22	25.90 ± 0.10	41.55 ± 0.10
$\text{tr}(\mathbf{A}_{\text{g}J})_\text{0e}/3 \cdot 10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	24.28 ± 0.01	14.79 ± 0.40	39.24 ± 0.14	61.48 ± 0.14
$[(\alpha_{\text{g}Jx})_\text{s}; (\alpha_{\text{g}Jy})_\text{s}; (\alpha_{\text{g}Jz})_\text{s}]/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	27.91; 27.91; 17.03	20.74; 14.87; 8.76	52.22; 45.74; 27.55	81.53; 75.05; 45.43
$\text{tr}(\boldsymbol{\alpha}_{\text{g}J})_\text{s}/3 \cdot 10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	24.28	14.79	41.84	67.34
$(\alpha_{\text{g}Jx})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	29.31 ± 0.03	22.91 ± 7.0	—	84.8 ± 3.5
$(\alpha_{\text{g}Jy})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	29.31 ± 0.03	16.43 ± 5.0	—	78.1 ± 3.2
$(\alpha_{\text{g}Jz})_\text{0e}/10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	17.88 ± 0.02	9.67 ± 3.0	—	47.3 ± 1.8
$\text{tr}(\boldsymbol{\alpha}_{\text{g}J})_\text{0e}/3 \cdot 10^{-40}\,\text{CV}^{-1}\,\text{m}^2$	25.50 ± 0.03	16.34 ± 5.0	—	70.0 ± 3.0
$(\mu_{\text{g}Jz})_\text{0e}/10^{-30}\,\text{Cm}$	0	0	7.0 ± 0.2	0 ± 2
$\Vert\boldsymbol{\mu}^*_{\text{ga}J}\Vert/10^{-30}\,\text{Cm}$	—	—	11.73 ± 0.22	14.15 ± 0.30
$\Vert(\boldsymbol{\mu}_{\text{ga}J})_\text{0e}\Vert/10^{-30}\,\text{Cm}$	—	—	11.25 ± 0.30	14.15 ± 0.30

Remark: The values of $(\alpha_{\text{g}J\lambda})_\text{0e}$, $\lambda = x, y, z$, $J = 2, 3, 21$, are estimated assuming $\boldsymbol{\mu}_{\text{g}J} = 0$ and $(\alpha_{\text{g}J\lambda})_\text{0e}/\text{tr}(\boldsymbol{\alpha}_{\text{g}J})_\text{0e} = (\alpha_{\text{g}J\lambda})_\text{s}/\text{tr}(\boldsymbol{\alpha}_{\text{g}J})_\text{s}$.

Table 12. For the determination of ζ^*_{11}, ζ'^*_{11}, ζ^*_{21} and ζ'^*_{21} a few of the coefficients $\lambda_{c\zeta I\alpha_1\alpha_2}$ and $\lambda_{c\zeta' I\alpha_1\alpha_2}$ give only a negligible contribution ($\lambda_{c\zeta 1.10}$, $\lambda_{c\zeta 1.20}$, $\lambda_{c\zeta 2.10}$, $\lambda_{c\zeta 2.01}$, $\lambda_{c\zeta 3.10}$, $\lambda_{c\zeta 3.20}$ and the corresponding $\lambda_{c\zeta' I.\alpha_1\alpha_2}$). But, as we want to emphasize, this does not hold true for the coefficients generally. The coefficient $\lambda_{c\zeta 1.11}$ contributes approximately 15% of the quantity $B_{c\mathsf{Z}1}$ to ζ^*_{11}; the coefficients $\lambda_{c\zeta 1.11}$ and $\lambda_{c\zeta 1.21}$ each contribute ten times as much to ζ^*_{21} as $B_{c\mathsf{Z}2}$, 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 $(a_{I\lambda})_\text{s}$, $I = 21$, $\lambda = x, y, z$, 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 $3.4 \cdot 10^{-10}$ 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 $(\mathbf{A}_\text{g21})_\text{b} = 2(\mathbf{A}_\text{g2})_\text{0e} + (\mathbf{A}_\text{g3})_\text{0e}$ and $(\boldsymbol{\alpha}_\text{g21})_\text{s} = 2(\boldsymbol{\alpha}_\text{g2})_\text{0e} + (\boldsymbol{\alpha}_\text{g3})_\text{0e}$ assuming the described configuration. With these data the evaluation of ζ^*_{21} and ζ'^*_{21} was done as above. The data used and the obtained values of $(\boldsymbol{\mu}_\text{g21})_\text{0e}$, $(\mathbf{A}_\text{g21})_\text{0e}$ and $(\boldsymbol{\alpha}_\text{g21})_\text{0e}$ are listed in Table 12.

Assuming model II — the formation of only the 1:1-complex — from the quantities $B_{c\mathsf{Z}2}$ and $B_{c\mathsf{Z}'2}$, Table 9, the values of the coefficients

$$\lambda_{c\zeta 11.10} = -(1.83 \pm 0.10) \cdot 10^{-6}\,\text{m}^6\,\text{mol}^{-2}$$

and

$$\lambda_{c\zeta' 11.10} = (2.8 \pm 1.1) \cdot 10^{-8}\,\text{m}^6\,\text{mol}^{-2}$$

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 CCl_4 at 293 K were also performed by Briegleb, Czekalla, and Reuss [16] in a concentration interval $c_{02}^{+} = 142$ to 275 mol m^{-3}, where the 2:1 complex formation is not negligible. Therefore the magnitude $\| \boldsymbol{\mu}_{g11} \|$ of the dipole moment estimated with the assumption of only 1:1 complex formation is expected to be erroneous ($4.50 \cdot 10^{-30}$ Cm). Their data have been evaluated again by Foster and Kulevsky [17], who estimated $\| \boldsymbol{\mu}_{g11} \| = (9.3 \pm 1.0) \cdot 10^{-30}$ and $\| \boldsymbol{\mu}_{g21} \| = (0 \pm 3.3) \cdot 10^{-30}$ 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_{02}^{+} investigated make it very improbable that any method of evaluation could lead to reliable values of $\| \boldsymbol{\mu}_{g11} \|$ and $\| \boldsymbol{\mu}_{g21} \|$ as may be recognized from the data of Briegleb et al. in Figure 3. From measurements in CCl_4 at 298 K but only taking the formation of the 1:1 complex into account, Chan and Liao [60] obtained $\| \boldsymbol{\mu}_{g11} \| = 5.5 \cdot 10^{-30}$ Cm.

4.4. Electro-Optical Absorption Measurements

The quantity M, defined by (I.166), characterizes the electro-optical absorption of isotropic solutions. These quantities were measured of eight solutions of HMB and TCNE in CCl_4 at 298.15 K at 20 wavenumbers in the interval $\tilde{\nu} = 1.56$ to $2.08 \cdot 10^6 \text{ m}^{-1}$ ($c_{02}^{+} = 8$ to 370 mol m^{-3}, $c_{03} = 0.04$ to 0.17 mol m^{-3}). The data obtained have shown that in the investigated concentration intervals the specific electro-optical absorption $\mathsf{P}_{w\mathsf{Y}} = M/\varrho$ is linearly dependent on w_{03} and in the investigated wavenumber interval the limit of $\mathsf{P}_{w\mathsf{Y}}$ for $w_{03} \to 0$ vanishes, i.e. $\mathsf{P}_{w\mathsf{Y}}^{+} = 0$. 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:

$$\mathsf{Y}_{03}^{+} = \left[\frac{1}{c_{03}} \lim_{E_a^2 \to 0} \left(\frac{\partial a_E}{\partial E_a^2} \right) \right]^{+} = \left(\frac{M}{c_{03}} \right)^{+} = \frac{M}{c_{03}}, \tag{53}$$

where a_E is the optical absorption coefficient of the solution in an applied electric field $\boldsymbol{E}_a$. At fixed values of T and p the PMQ Y_{03}^{+} depends on c_{02}^{+}, $\tilde{\nu}$ and χ, where χ is the angle between $\boldsymbol{E}_a$ and the polarization direction $\boldsymbol{e}$ 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 χ and variable values of c_{02}^{+} satisfies (19), but in this case three coefficients $B_{c\mathsf{Y}\alpha}$ are not sufficient for an appropriate representation as will be shortly recognized.

Since under the considered conditions $\varkappa_1 = \varkappa_2 = \varkappa_3 = 0$ we may safely assume $v_1 = v_2 = v_3 = 0$, where v_I is the model molar electro-optical absorption of the molecule A_I, compare (III.2). Furthermore it is $\lambda_{cvI.\alpha_1\alpha_2} = 0$, for $I = 1, 2$ and 3. For model I the coefficients $\eta_{c11.10}$ and $\lambda_{c\varkappa11.10}$ are vanishingly small, as has been shown in Sect. 4.1, and therefore $\lambda_{cv11.10}$ and the field dependence of $\eta_{c11.10}$ are negligible. With these presuppositions from (19) to (24) follows for the limit of (a_E/c_{03}) in an applied electric field

$$\left(\frac{a_E}{c_{E03}} \right)^{+} = \frac{\varkappa_{E11}^{*} K_{Ec11}^{*} c_{E02}^{+} (c^{\ominus})^{-1} + \varkappa_{E21}^{*} K_{Ec21}^{*} (c_{E02}^{+})^2 (c^{\ominus})^{-2}}{1 + K_{Ec11}^{*} c_{E02}^{+} (c^{\ominus})^{-1} + K_{Ec21}^{*} (c_{E02}^{+})^2 (c^{\ominus})^2}, \tag{54}$$

Table 13. Values of the limit Y_{03}^{+} of the partial molar electro-optical absorption of TCNE in solutions of HMB and TCNE in CCl_4 at 298.15 K.

c_{02}^{+}/mol $\cdot \text{m}^{-3}$	8.134		23.972		32.097		52.375		113.262		162.542		360.880		371.884	
	$\mathsf{Y}_{03}^{+}(\tilde{\nu}, \chi)/10^{-19} \text{ m}^4 \text{ V}^{-2} \text{ mol}^{-1}$															
$\tilde{\nu}/10^4 \text{m}^{-1}$ χ	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	$\pi/2$
156	2457	718	3211	765	3354	840	3515	847	3514	873	3483	927	3401	1023	3401	977
160	2785	715	3482	654	3603	706	3648	643	3474	665	3403	683	3128	725	3067	717
164	2999	677	3509	423	3615	493	3432	287	2815	139	2551	115	2028	108	1941	124
168	3144	664	3522	241	3481	190	3126	−70	2289	−340	1863	−422	1043	−489	903	−507
172	3245	594	3544	81	3542	7	3113	−414	2150	−659	1726	−732	820	−795	717	−791
176	3306	536	3606	−61	3566	−163	3190	−560	2306	−769	1900	−840	1062	−890	1026	−835

where the indices "E" are used to designate quantities in an applied electric field. The quantities [36]

$$L_J^* = \left[\frac{1}{\varkappa_J} \lim_{E_a{}^2 \to 0} \left(\frac{\partial \varkappa_{EJ}}{\partial E_\mathrm{a}^2}\right)_{n_{0I},\, \vartheta_\iota}\right]^*, \tag{55}$$

$$q_J'^* = \left[\frac{1}{c_{0J}} \lim_{E_a{}^2 \to 0} \left(\frac{\partial c_{E0J}}{\partial E_\mathrm{a}^2}\right)_{n_{0I},\, \vartheta_\iota}\right]^*, \tag{56}$$

$$p_{\lambda\nu}^* = \left[\frac{1}{K_{c\lambda\nu}} \lim_{E_a{}^2 \to 0} \left(\frac{\partial K_{Ec\lambda\nu}}{\partial E_\mathrm{a}^2}\right)_{n_{0I},\, \vartheta_\iota}\right]^* \tag{57}$$

are introduced to describe the field dependence of the molar absorption coefficients $\varkappa_{EJ}$, the initial concentrations c_{E0J} of the substances used to generate the solution, and the equilibrium constants $K_{Ec\lambda\nu}$ of the occurring chemical reactions. With (54) to (57) follows from (53)

$$\begin{aligned} \mathsf{Y}_{03}^+ = {} & [1 + K_{c11}^* c_{02}^+ (c^\ominus)^{-1} + K_{c21}^* (c_{02}^+)^2 (c^\ominus)^{-2}]^{-1} \\ & \cdot \{(L_{11}^* + q_3'^*)\, \varkappa_{11}^* K_{c11}^* c_{02}^+ (c^\ominus)^{-1} \\ & + (L_{21}^* + q_3'^*)\, \varkappa_{21}^* K_{c21}^* (c_{02}^+)^2 (c^\ominus)^{-2} \\ & + (p_{11}^* + q_2'^*)(\varkappa_{11}^* - \mathsf{K}_{03}^+) K_{c11}^* c_{02}^+ (c^\ominus)^{-1} \\ & + (p_{21}^* + 2\, q_2'^*)(\varkappa_{21}^* - \mathsf{K}_{03}^+) K_{c21}^* (c_{02}^+)^2 (c^\ominus)^{-2}\}\,. \end{aligned} \tag{58}$$

In the last two terms of the second bracket are the partial molar absorptions K_{03}^+ which cause a rather complicated dependence of Y_{03}^+ on c_{02}^+ and therefore the application of the formal expansion, Eq. (19), is not appropriate.

The quantities $L_J^*(\tilde{\nu}, \chi)$ are related to the transition dipole moment $\boldsymbol{\mu}_{\mathrm{ga}J}$ and to the electric dipole moments $\boldsymbol{\mu}_{\mathrm{g}J}$ and $\boldsymbol{\mu}_{\mathrm{a}J}$ and the polarizabilities $\boldsymbol{\alpha}_{\mathrm{g}J}$ and $\boldsymbol{\alpha}_{\mathrm{a}J}$ 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_J^* on $\tilde{\nu}$ and χ leads to quantities D^* to I^*, compare (III.6) to (III.10). From D^* to I^* in favorable cases information about $\boldsymbol{\mu}_{\mathrm{g}J}$, $\boldsymbol{\mu}_{\mathrm{a}J}$, $\boldsymbol{\alpha}_{\mathrm{g}J}$, $\boldsymbol{\alpha}_{\mathrm{a}J}$ and $\boldsymbol{\mu}_{\mathrm{ga}J}$ 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 $1 \cdot 10^{-21}\,\mathrm{V}^{-2}\,\mathrm{m}^2$, which can be neglected compared to the errors of measured values of L_J^*. 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 $q_2'^*$ and $q_3'^*$ may safely be neglected in (58).

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

$$RT \ln K_{Ec\lambda\nu}^* = -\,(g_{Ec\lambda\nu}^* - \lambda\, g_{Ec2}^* - \tilde{\nu}\, g_{Ec3}^*)\,, \tag{59}$$

where g_{EcJ}^* is the model molar Gibbs energy of the substance A_J in the solution in an applied electric field, which can be represented as*

$$\begin{aligned} g_{EcJ}^* = g_{cJ}^* - {} & \frac{E_\mathrm{a}^2 N_\mathrm{A}}{6} \\ & \cdot [(kT)^{-1} \tilde{\boldsymbol{\mu}}_{\mathrm{g}J} (\mathbf{1} - \mathbf{f}_J^* \boldsymbol{\alpha}_{\mathrm{g}J})^{-2} \mathbf{f}_{\mathrm{e}J}^{*2} \boldsymbol{\mu}_{\mathrm{g}J} \\ & + \mathrm{tr}\, \{(\mathbf{1} - \mathbf{f}_J^* \boldsymbol{\alpha}_{\mathrm{g}J})^{-1} \boldsymbol{\alpha}_{\mathrm{g}J} \mathbf{f}_{\mathrm{e}J}^{*2}\}]\,, \end{aligned} \tag{60}$$

where g_{cJ}^* is the model molar Gibbs energy of A_J in absence of an applied field and the tensors $\mathbf{f}_{\mathrm{e}J}^*$ and $\mathbf{f}_J^*$ are defined by (II.34) and (II.35), respectively. Introducing (59) and (60) into (57) leads to

$$\begin{aligned} p_{\lambda\nu}^* = {} & \frac{1}{6\,kT} \sum_{J=1}^{K} \tilde{\nu}_{\lambda\nu J} \\ & \cdot [(kT)^{-1} \tilde{\boldsymbol{\mu}}_{\mathrm{g}J} (\mathbf{1} - \mathbf{f}_J^* \boldsymbol{\alpha}_{\mathrm{g}J})^{-2} \mathbf{f}_{\mathrm{e}J}^{*2} \boldsymbol{\mu}_{\mathrm{g}J} \\ & + \mathrm{tr}\, \{(\mathbf{1} - \mathbf{f}_J^* \boldsymbol{\alpha}_{\mathrm{g}J})^{-1} \boldsymbol{\alpha}_{\mathrm{g}J} \mathbf{f}_{\mathrm{e}J}^{*2}\}]\,. \end{aligned} \tag{61}$$

With the values obtained in Sect. 4.3 the values of p_{11}^* and p_{21}^* are calculated as listed in Table 14.

Considering the quantities c_{02}^+, K_{c11}^*, K_{c21}^*, $\varkappa_{11}^*$, $\varkappa_{21}^*$ and K_{03}^+, whose values can be calculated using (19) and the data obtained in Sect. 4.1, as known quantities, and neglecting $q_2'^*$ and $q_3'^*$, analysis of variance according to (58) shows that the coefficients $L_{11}^* \varkappa_{11}^*$, $L_{21}^* \varkappa_{21}^*$ and p_{11}^* may be estimated from available 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 $p_{21}^* = 50.9 \cdot 10^{-20}\, V^{-2}\,\mathrm{m}^2$ as known quantity. Multiple regression according to (58) leads to an estimator for p_{11}^*, namely $(p_{11}^*)_\mathrm{estim} = (102 \pm 6) \cdot 10^{-20}\,\mathrm{V}^{-2}\,\mathrm{m}^2$. 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 $p_{11}^* = 103.8 \cdot 10^{-20}\,\mathrm{V}^{-2}\,\mathrm{m}^2$ as known, multiple re-

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* Compare (131) [53], for example, after averaging over all orientations in the applied field.

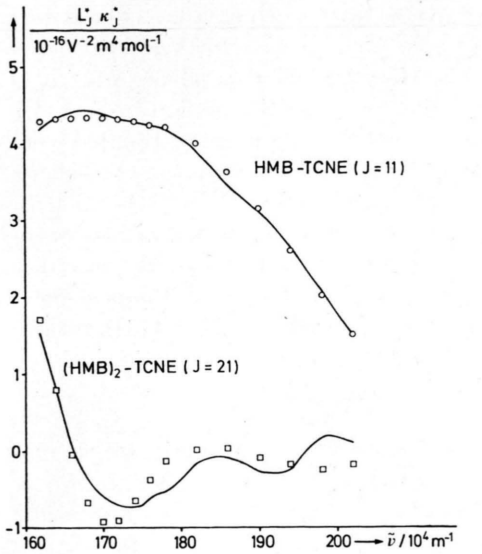

Fig. 4. Values of $L_{11}^* \varkappa_{11}^*$ and $L_{21}^* \varkappa_{21}^*$ at $\chi = 0$ of the complexes HMB-TCNE and $(HMB)_2$-TCNE in CCl_4 at 298.15 K. The curves are calculated using (58) and the data in Tables 4, 5 and 14.

gression according to (58) allows to estimate the values of $\varkappa_{11}^* L_{11}^*$ and $\varkappa_{21}^* L_{21}^*$ at $\chi = 0$ and $\pi/2$; they are represented in Figs. 4 and 5.

The values of $L_I^* \varkappa_I^*$ $(I = 11, 21)$ depend on $\tilde{\nu}$ and χ 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 $Q^{(i)}(\boldsymbol{E}_f)$, $i = 1, \ldots, 5$, can safely be neglected as well as $S^{(1)}$ and $S^{(2)}$ (an assumption confirmed by the very small value of D_{21}^*). Since the values of F_{11}^* and G_{11}^* and the values of H_{11}^* and I_{11}^* are almost equal, the dipole moments $\boldsymbol{\mu}_{g11}$ and $\boldsymbol{\mu}_{a11}$ and the transition dipole moment $\boldsymbol{\mu}_{ga11}$ (with $\boldsymbol{m} = \boldsymbol{\mu}_{ga11}/\|\boldsymbol{\mu}_{ga11}\|$) 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}. From the values of D_{11}^* and E_{11}^* the quantities $R_{011z}^{(1)}$ and $R_{021z}^{(2)}$ may be estimated according to (III.11) and (III.12) and therefrom the components $(\alpha_{ag11})_{zz}$ and $(\alpha_{ag11})_{xx} + (\alpha_{ag11})_{yy}$ of the transition polarizability follow, if (35) and (36) of a previous paper [55] are used; the data are listed in Table 14. The errors of the quantities H_{11}^* and I_{11}^* prohibit an estimation of the change of the polarizability of the HMB-TCNE complex during the considered excitation process.

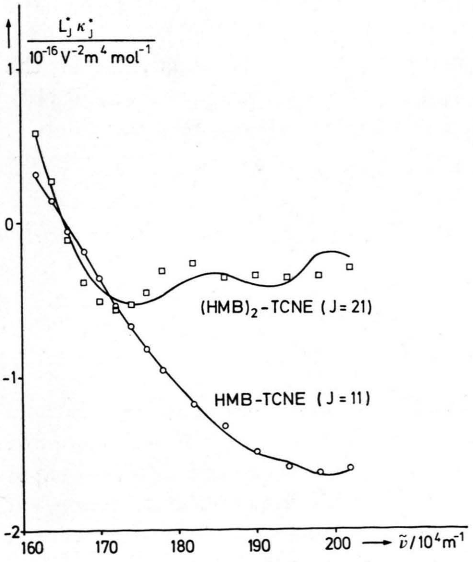

Fig. 5. Values of $L_{11}^* \varkappa_{11}^*$ and $L_{21}^* \varkappa_{21}^*$ at $\chi = \pi/2$ of the complexes HMB-TCNE and $(HMB)_2$-TCNE in CCl_4 at 298.15 K. The curves are calculated using (58) and the data in Tables 4, 5 and 14.

Table 14. Evaluation of the electro-optical absorption measurements for solutions in CCl_4 at $T = 298.15$ K.

J	Remark	HMB-TCNE 11	$(HMB)_2$-TCNE 21
$p_J^*/10^{-20}\,V^{-2}\,m^2$		103.8	50.9
$D_J^*/10^{-20}\,V^{-2}\,m^2$		40.7 ± 5.1	9 ± 8
$E_J^*/10^{-20}\,V^{-2}\,m^2$		1216 ± 30	120 ± 80
$F_J^*/10^{-40}\,CV^{-1}\,m^2$		496 ± 16	91 ± 30
$G_J^*/10^{-40}\,CV^{-1}\,m^2$		480 ± 16	69 ± 30
$H_J^*/10^{-60}\,C^2\,m^2$		690 ± 230	960 ± 210
$I_J^*/10^{-60}\,C^2\,m^2$		620 ± 230	860 ± 210
$R_{0Jz}^{(1)}/10^{-10}\,V^{-1}\,m$		1.12 ± 0.14	—
$R_{0Jz}^{(2)}/10^{-10}\,V^{-1}\,m$		1.26 ± 0.68	—
$(\alpha_{agJ})_{zz}/10^{-40}\,CV^{-1}\,m^2$		6.5 ± 1.0	—
$((\alpha_{gaJ})_{xx} + (\alpha_{agJ})_{yy})/10^{-40}\,CV^{-1}\,m^2$		-6 ± 6	—
$\mu_{aJz}/10^{-30}\,Cm$	(1)	19.8 ± 0.8	—
$\mu_{aJz}/10^{-30}\,Cm$	(2)	24 ± 4	22 ± 4
$\mu_{aJz}/10^{-30}\,Cm$	(3)	—	19.8 ± 3.0
$\alpha_{aJz}/10^{-40}\,CV^{-1}\,m^2$	(3)	—	89 ± 30
$(\alpha_{aJx} + \alpha_{aJy})/10^{-40}\,CV^{-1}\,m^2$	(3)	—	195 ± 40

Remarks:

(1) Estimated from F and G assuming $\boldsymbol{\alpha}_{aJ} = \boldsymbol{\alpha}_{gJ}$.
(2) Estimated from H and I assuming $\boldsymbol{\alpha}_{aJ} = \boldsymbol{\alpha}_{gJ}$.
(3) Estimated from F, G, H and I with the presuppositions $\mu_{g21z} = 0$, $R_{021z}^{(1)} = R_{011z}^{(1)}$ and $R_{021z}^{(2)} = R_{011z}^{(2)}$.

Assuming $\boldsymbol{\alpha}_{\mathrm{a}11} = \boldsymbol{\alpha}_{\mathrm{g}11}$, the value of the magnitude of the dipole moment $\| \boldsymbol{\mu}_{\mathrm{a}11} \|$ in the excited state can be obtained from F_{11}^* and G_{11}^* and Eqs. (III.13) and (III.14) with a rather good accuracy and from H_{11}^* and I_{11}^* 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 $\| \boldsymbol{\mu}_{\mathrm{a}11} \|$ would be approximately 20% smaller. Hence one may expect a reliability of the reported value of $\| \boldsymbol{\mu}_{\mathrm{a}11} \|$ of the same order.

Due to the intricate evaluation of data the quantities $L_{21}^* \varkappa_{21}^*$ of the (HMB)$_2$-TCNE complex are less accurate than the quantities $L_{11}^* \varkappa_{11}^*$ of the HMB-TCNE complex as may be recognized from Figs. 4 and 5, and hence the quantities $D_{21}^*, \ldots, I_{21}^*$ are less reliable than the corresponding quantities $D_{11}^*, \ldots, I_{11}^*$. The values of D_{21}^* and E_{21}^* 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_{21}^* and I_{21}^* follows a large magnitude of the electric dipole moment $\boldsymbol{\mu}_{\mathrm{a}21}$ of the 2:1 complex in its excited state. The equality of H_{21}^* and I_{21}^* shows that $\boldsymbol{\mu}_{\mathrm{a}21}$ is parallel to the direction $\boldsymbol{m}_{21} = \boldsymbol{\mu}_{\mathrm{ga}21} / \| \boldsymbol{\mu}_{\mathrm{ga}21} \|$ of the transition dipole moment. Assuming $\boldsymbol{\alpha}_{\mathrm{a}21} = \boldsymbol{\alpha}_{\mathrm{g}21}$ leads to the value of $\mu_{\mathrm{a}21z}$ 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_{21}^* and G_{21}^* confirm the very small value of the magnitude of the dipole moment in the electronic ground state: $\| \boldsymbol{\mu}_{\mathrm{g}21} \| < 1 \cdot 10^{-30}$ Cm (compare Section 4.3). With the presuppositions $\mu_{\mathrm{g}21z} = 0$, $R_{021z}^{(1)} = R_{011z}^{(1)}$ and $R_{021z}^{(2)} = R_{011z}^{(2)}$ from F_{21}^*, G_{21}^*, H_{21}^* and I_{21}^* the quantities $\mu_{\mathrm{a}21z}$, $\alpha_{\mathrm{a}21z}$ and $\alpha_{\mathrm{a}21x} + \alpha_{\mathrm{a}21y}$ can be estimated; the values are listed in Table 14. The dipole moment $\mu_{\mathrm{a}21z}$ of the 2:1 complex in the excited state is nearly equal to the change $\mu_{\mathrm{a}11z} - \mu_{\mathrm{g}11z}$ 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_{11}^*, p_{11}^* and two further coefficients describing the electric field dependence of $\eta_{c11.10}$ and $\lambda_{c\varkappa 11.10}$. 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 $\eta_{c11.10}$ and $\lambda_{c\varkappa 11.10}$ based on (31) and (37), respectively, furthermore show that the corresponding coefficients are negligibly small compared to L_{21}^* and p_{21}^*.

The first determination of an electric dipole moment of an EDA complex in its excited state was done by Czekalla 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 μ^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 $\| \boldsymbol{\mu}_{\mathrm{a}11} \| = 32 \cdot 10^{-30}$ 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

$$D_{11} = 39 \cdot 10^{-20}\ \mathrm{V}^{-2}\,\mathrm{m}^2,$$
$$E_{11} = 746 \cdot 10^{-20}\ \mathrm{V}^{-2}\,\mathrm{m}^2,$$
$$F_{11} = 223 \cdot 10^{-40}\ \mathrm{CV}^{-1}\,\mathrm{m}^2,$$
$$G_{11} = 193 \cdot 10^{-40}\ \mathrm{CV}^{-1}\,\mathrm{m}^2,$$
$$H_{11} = 568 \cdot 10^{-60}\ \mathrm{C}^2\,\mathrm{m}^2 \quad \text{and}$$
$$I_{11} = 590 \cdot 10^{-60}\ \mathrm{C}^2\,\mathrm{m}^2$$

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 $p_{11}^* = 0$ (and naturally $p_{21}^* = 0$), 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 $(HMB)_2$-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 ($\lambda_{c\varkappa 11.10}$), the model molar refractions ($\lambda_{c\zeta' 11.10}$), the model molar electric susceptibilities ($\lambda_{c\zeta 11.10}$) and the coefficients describing the electric field dependence of $\eta_{c11.10}$ and $\lambda_{c\varkappa 11.10}$ 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 $\boldsymbol{\mu}_{\mathrm{ga}11}$ is parallel to the two-fold rotation axis of the complex, and hence the first excited state, corresponding to the excitation at $\tilde{\nu} = 186 \cdot 10^4 \mathrm{~m}^{-1}$, is a A_1 state as well as the ground state of the complex. The magnitude of the electric dipole moment is $\| \boldsymbol{\mu}_{\mathrm{g}11} \| = 7.0 \cdot 10^{-30}$ Cm in the ground state, the direction of $\boldsymbol{\mu}_{\mathrm{g}11}$ is from the TCNE group to the HMB group of the complex. The magnitude of the dipole moment is $\| \boldsymbol{\mu}_{\mathrm{a}11} \| = 19 \cdot 10^{-30}$ Cm in the considered excited state, and the directions of $\boldsymbol{\mu}_{\mathrm{g}11}$ and $\boldsymbol{\mu}_{\mathrm{a}11}$ 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 $(HMB)_2$-TCNE complex exhibits an optical absorption band with maximum at $184 \cdot 10^4 \mathrm{~m}^{-1}$ 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 $(HMB)_2$-TCNE complex in its electronic ground state is either zero or nearly zero ($\| \boldsymbol{\mu}_{\mathrm{g}21} \| < 1 \cdot 10^{-30}$ 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 $\Delta_R h_c^*$ 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 $\Delta\tilde{\nu} = -4.6 \cdot 10^4\ \mathrm{m}^{-1}$ for the 1:1 complex and $\Delta\tilde{\nu} = -2.9 \cdot 10^4\ \mathrm{m}^{-1}$ 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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