Charge-Transfer Complexes and Reactivity in Diels-Alder Cycloadditions

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The reactivity of 2,3-bis(methylene)norbornane (**1**) towards the highly reactive dienophiles 2,3-dicyano-*p*-benzoquinone (**2**), tetracyanoethylene (**3**), 2,3-dicyanomaleimide (**4**), and *p*-benzoquinone-2,3-dicarboxylic anhydride (**5**) was analysed kinetically. CT complexes were observed for **1** with **2**–**5** and equilibrium constants for the formation of the CT complexes between **1** and **2**–**4** were determined kinetically. The relationship between relative rates, CT-excitation energies, HOMO-LUMO separations, and CT-complex equilibrium constants is discussed. The results do not require the CT complexes to be intermediates but strongly support the importance of CT interactions in the transition state of these cycloadditions.

Charge-Transfer-Komplexe und Reaktivität bei Diels-Alder-Reaktionen

Die Reaktivität von 2,3-Bis(methylen)norbornan (**1**) gegenüber 2,3-Dicyan-*p*-benzochinon (**2**), Tetracyanethylen (**3**), 2,3-Dicyanmaleinsäureimid (**4**) und *p*-Benzochinon-2,3-dicarbonsäureanhydrid (**5**) wurde kinetisch untersucht. Zwischen **1** und **2**–**5** konnten CT-Komplexe nachgewiesen werden. Die Gleichgewichtskonstanten der Komplexbildung zwischen Dien **1** und den Dienophilen **2**–**4** wurden kinetisch ermittelt. Der Zusammenhang zwischen relativer Geschwindigkeit, CT-Anregungsenergien, HOMO-LUMO-Abständen und den Gleichgewichtskonstanten der CT-Komplexbildung wird analysiert. Aus den Ergebnissen kann nicht auf CT-Komplexe als Zwischenstufen der Diels-Alder-Reaktionen geschlossen werden, vielmehr zeigen sie die große Bedeutung von CT-Wechselwirkungen für die Übergangszustände der Reaktionen.

In 1952 Mulliken[1] formulated the theory of charge-transfer complexes to explain the existence of weak molecular complexes between molecules with electron donor and electron acceptor properties. A great number of compounds of different chemical nature are able to form such complexes[2]. Apart from the study of their properties, their significance as intermediates in chemical reactions has been discussed very early[3]. In 1948 Bachmann and Scott[4] suggested that they might be necessary intermediates in Diels-Alder reactions. It was in 1955 that Andrews and Keefer analysed kinetically CT complexes between anthracene as potential diene in a Diels-Alder cycloaddition and the electron-deficient dienophile maleic anhydride[5]. As outlined by these authors there are two possibilities to account for the CT complex in the [4 + 2] cycloaddition (Scheme 1). Unfortunately kinetic measurements do not allow a distinction between the case where the CT complex is an intermediate on the reaction coordinate for cycloaddition (eq. 1) and where the complex exists as a non-reactive species in equilibrium with the diene and the dienophile (eq. 2).

Scheme 1

$$\mathrm{D + A} \overset{K}{\rightleftharpoons} \text{CT complex} \xrightarrow{k'_1} \text{cycloadduct} \qquad (1)$$

$$\text{CT complex} \overset{K}{\rightleftharpoons} \mathrm{D + A} \xrightarrow{k_1} \text{cycloadduct} \qquad (2)$$

D = diene (electron donor)
A = dienophile (electron acceptor)

A number of attempts has been made over the years to prove or disprove such complexes as reaction intermediates[3]. Equilibrium constants for complex formation between substituted anthracenes with chloroanil and between substituted maleimides and maleic anhydride with hexamethylbenzene were determined. The logarithms of the stability constants of these complexes and of the rate constants of the cycloaddition between substituted anthracenes and maleic anhydride as well as between cyclopentadiene and substituted maleimides show a linear correlation that was taken as evidence that CT complexes are involved in the reaction mechanism[6]. In another study the rate constants of the cycloadditions of tetracyanoethylene to 1,2- and 9-substituted anthracenes has been compared with the equilibrium constants for CT-complex formation between these dienes and the dienophile[7]. In some cases the visual observation of CT complexes between the diene and the dienophile has been taken as sufficient evidence for their involvement in the cycloaddition[8].

An important contribution in this area was provided by Kiselev and Miller[9]. However, the uncritical application of this singular result to Diels-Alder cycloadditions in general has also caused confusion. For the cycloaddition of 9,10-dimethylanthracene to tetracyanoethylene they observed a negative activation enthalpy in some solvents and interpreted this in terms of a complex formation prior to cycloaddition, the shape of the reaction coordinate being as in Figure 1. A negative activation enthalpy can be explained by this reaction coordinate and in this case complex formation has indeed kinetic significance for the reaction. If, however, the activation enthalpy is positive and greater than the absolute value of the enthalpy of complex formation then the complex has no kinetic significance for the cycloaddition. The question may be whether in this case it is more important to devise experiments in order to prove the type of reaction coordinate of Figure 2 or whether it might be more appropriate to ask what the significance of the occurrence of CT complexes for the reactivity in these cycloadditions could be? Even for the case of negative activation enthalpies in chemical reactions it has been questioned[10] that these have to be interpreted in terms of a precomplex formation.

Recently, the problem of CT complexes in [4 + 2] cycloadditions has been discussed in the context of single electron transfer in the transition state. From a study of the CT-absorption spectra and the rates of cycloadditions between various anthracenes and tetra-

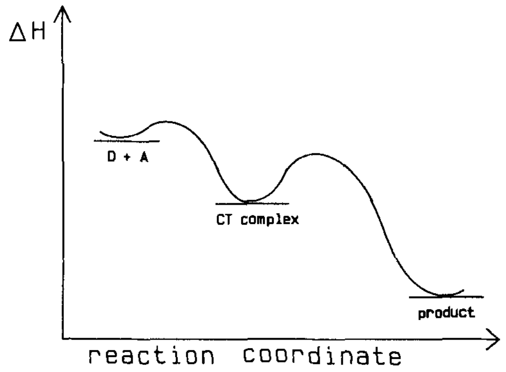


Figure 1. Reaction coordinate for the cycloaddition of 9,10-dimethylanthracene to tetracyanoethylene

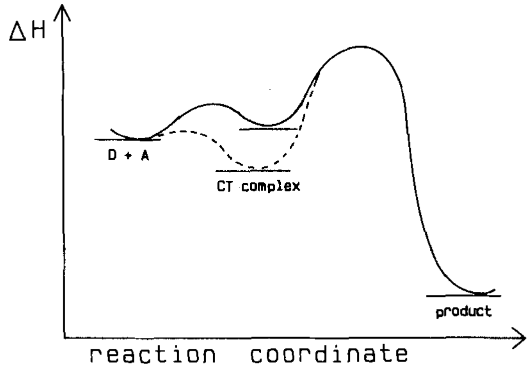
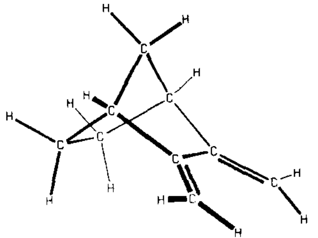


Figure 2. Reaction coordinate for a typical Diels-Alder reaction ($\Delta H^{\neq} > 0$) with possible formation of a CT complex

cyanoethylene it was concluded that electron transfer should be important in the transition state[11,12]. The failure[13] to observe a cycloaddition after formation of radical ion pairs by laser excitation of CT bands in complexes between substituted anthracenes and tetracyanoethylene casts doubts on a complete electron transfer in the cycloaddition process. Single electron transfer in Diels-Alder cycloadditions seems to be feasible only under special circumstances[14]. The existence of CT complexes, however, may nevertheless be important for the cycloaddition. They are the manifestation of charge-transfer interactions which in turn are necessary for the formation of new covalent bonds[15,16].

A survey of the literature on the observation of CT complexes in Diels-Alder reactions discloses that the dienes are, without exception, molecules with aromatic rings, being either condensed aromatics or carrying phenyl groups as substituents. Charge-transfer complexes are the result of rather weak interactions and, therefore, their structure in solution should be loose. If one invokes them, as is often done, as important for regio- and stereoselectivity[17] one implies, mostly unconsciously, a structure in which the reaction centers of diene and dienophile are positioned above each other as in the assumed transition state. The presumption is that on the way to the transition state this preorientation will not be lost anymore. This, however, should be true only for the type of reaction coordinate of Figure 1. Furthermore, as in the observed CT complexes the diene is part of an extended aromatic π system there exists ample ambiguity as far as the structure of these complexes is concerned. Perhaps in the future, crystal structures of isolated CT complexes will shed some light on this problem[18].

Some time ago we decided to investigate the possible existence of CT complexes between an aliphatic diene (**1**) and a series of electron-deficient dienophiles (**2**–**5**). Diene **1** was chosen because it has the diene part fixed in a cisoid manner and, therefore, in the arrangement which is thought necessary for the cycloaddition. The assumption that the structure of possible CT complexes between **1** and the dienophiles **2**–**5** resembles the postulated transition state seemed to be more probable than in other cases. In connection with kinetic measurements and a perturbational MO analysis[19] we intended to gain insight into the course of these reactions.



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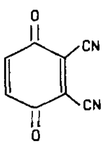

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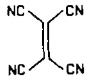

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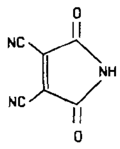

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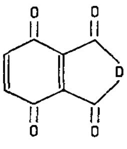

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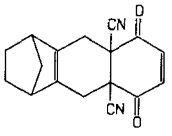
Preparative Aspects

Equimolar amounts of 2,3-bis(methylene)norbornane (**1**) and the dienophiles **2**, **4**, and **5** reacted at room temperature in methylene chloride or dioxane in essentially quantitative yields to give cycloaddition products. The reaction of **1** with tetracyanoethylene (**3**) has been described before[20]. According to ^{1}H-NMR and ^{13}C-NMR spectra of the crude reaction mixtures the cycloadducts **6**–**8** are mixtures of stereoisomers. No attempt was made to separate the isomers. By recrystallisation we obtained normally one of the compounds in enriched form.



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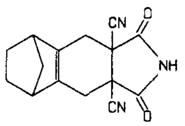

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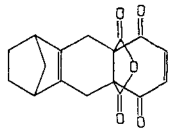

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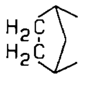
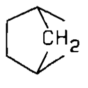
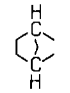
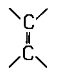
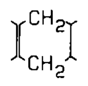
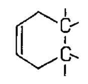
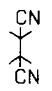
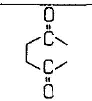
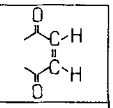
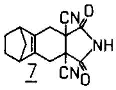
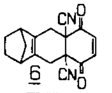
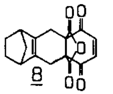
The interpretation of the ^{13}C-NMR data is described (Table 1) in order to exemplify the structure determination and to demonstrate the presence of a mixture of isomers. Two sets of signals (A and B) with a mean separation of individual lines of $\Delta\delta = 0.2-1.8$ are observed in each case. The classification of the signals in two sets, each belonging to one isomer, is possible because recrystallisation of the initial product mixtures leads generally to a change in isomer composition and by comparison of the ^{13}C-NMR spectra of crude and recrystallized products an unambiguous association can be made. The assignment of individual

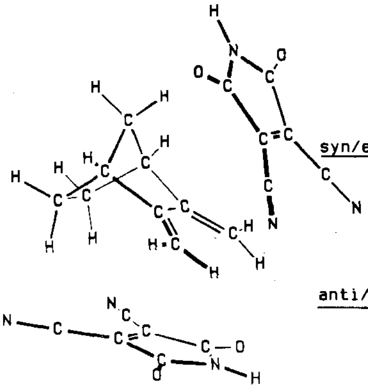
Table 1. ^{13}C-NMR data for Diels-Alder adducts **6**–**8** in CD_3CN as solvent. TMS internal standard, δ units, partially decoupled spectra. A = major isomer, B = minor isomer

										
 7	A	25.7(m)	48.2(t)	45.9(d)	138.4(s)	30.4(t)	49.1(s)	116.7(s)	170.5(s)	
	B	25.8(m)	48.4(t)	46.3(d)	138.8(s)	31.6(t)	49.9(s)	116.8(s)	170.7(s)	
 6	A	25.8(t)	47.3(t)	45.7(d)	136.0(s)	29.1(t)	53.4(s)	117.0(s)	187.6(s)	139.2(d)
	B	26.0(t)	47.3(t)	45.7(d)	135.7(s)	29.4(t)	53.7(s)	116.8(s)	187.6(s)	139.4(d)
 8	A	25.6(t)	46.4(t)	45.03(d)	135.7(s)	25.9(t)	60.7(s)	166.7(s)[a]	187.7(s)	138.7(d)
	B	25.5(t)	46.2(t)	44.98(d)	135.8(s)	26.3(t)	60.6(s)	166.6(s)[a]	187.6(s)	138.9(d)

[a] Angular C=O groups.

signals to specific carbon atoms rests on a comparison with the ^{13}C-NMR spectrum of norbornene and with spectral data in the literature[21].

The formation of a mixture of stereoisomers can be explained in two different ways. Due to the structure of **1** the dienophile, shown in **9** and **10** for **4**, can approach *endo* or *exo* with respect to the cyano groups from below the diene system giving products **11** and **12**. Depending on the mode of approach the stereoisomeric mixture may also result from *syn* or *anti* attack of the dienophile (**9** and **10**) from above or below the plane of the diene. The nature of the diene does not allow a distinction between these two possibilities.



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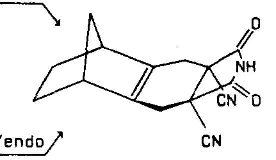

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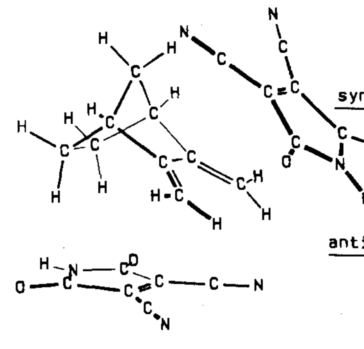

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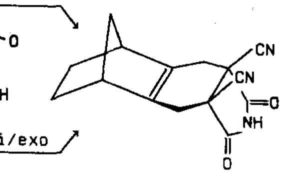

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Dienophiles **2** and **5** possess two dienophilic double bonds which might undergo cycloaddition. As follows from the ^{13}C-NMR data, reaction takes place in both cases only at the more highly substituted double bond. This is in accordance with other cycloadditions of these quinones[22].

Charge-Transfer Complexes

Charge-transfer complexes are identified by their absorption spectra in the visible or UV region. Compared with allowed intramolecular transitions these bands are characterised by low intensities and by maxima which occur at longer wavelengths than any of the absorption bands of the individual components. Due to the high reactivity of **2**–**5** towards **1** we expected, if at all, only transient absorptions of CT complexes. In order to realize experimental conditions for the detection of CT bands it was necessary to slow down the cycloaddition. This was achieved by decreasing the temperature to −90°C using specifically designed low temperature UV equipment (see Experimental). Because of the low solubility of 2,3-dicyanomaleimide (**4**) and of benzoquinone-2,3-dicarboxylic anhydride (**5**) in methylene chloride we also

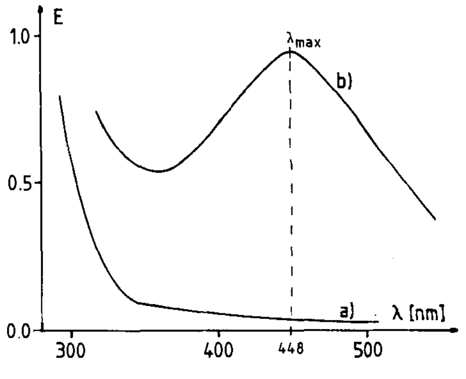

Figure 3. CT absorption for the complex of **1** with **3** at −90°C in CH_2Cl_2. a) absorption of the dienophile, b) after addition of an equimolar amount of **1**

used the less advantageous tetrahydrofuran as solvent. The latter solvent could have complicated the measurements because of its ability to form CT complexes with strong electron acceptors. Fortunately, however, this did not turn out to be a hampering problem.

If equimolar amounts, 4.7×10^{-2} M each, of **1** and tetracyanoethylene in methylene chloride are mixed at $-90\,^{\circ}$C a new absorption maximum at $\lambda_{max} = 448$ nm is recognized (Figure 3). Neither the individual components nor the cycloadduct show absorptions at this wavelength.

This band disappears even at $-90\,^{\circ}$C within 10 minutes and is attributed to a CT absorption between diene and dienophile. In THF as solvent the CT absorption is not as well separated from the CT absorptions between the dienophiles and the solvent. In that case its λ_{max} value was obtained by subtracting the composite spectrum from those of the individual components. Also this additional absorption disappeared within 10 to 15 minutes at $-90\,^{\circ}$C.

Similar to the procedure described for tetracyanoethylene we measured spectra of mixtures of **1** with **2**, **4**, and **5** at $-90\,^{\circ}$C. Transient absorptions were detected in all cases. The accuracy of their λ_{max} values is not very high in some cases and a range has to be given because absorptions for the individual molecules and the transient absorption are not well separated and the intensity of the additional transient absorption is not very high. Table 2 collects the results of these measurements and indicates the method of determination of the absorption maximum. In conclusion we can state that it is possible to detect CT absorptions for complexes between a simple aliphatic diene and strong electron acceptors.

Table 2. CT absorptions (λ_{max}) of mixtures of 2,3-bis(methylene)norbornane (**1**) and dienophiles **2**–**5** at $-90\,^{\circ}$C in a) methylene chloride and b) tetrahydrofuran (optical pathway 10 mm)

Dienophile	Conc. (mol/l)	λ_{max} (nm)	Method[c]	Lifetime of the complex T(°C)/t(min))
3	a) $4.7 \cdot 10^{-2}$	448	A	−90/10
	b) $1.0 \cdot 10^{-1}$	428	B	−90/15
4	b) $1.0 \cdot 10^{-1}$	420	B	−80/5
2	a) $4.2 \cdot 10^{-2}$	528–520	B	−90/15
	b) $1.0 \cdot 10^{-1}$	460–450	C	−90/15
5	b) $5.2 \cdot 10^{-2}$	480–450	C	−90/5

[c] Methods of determination of λ_{max}: A = Direct determination, CT band completely separated from individual absorptions, B = substraction of absorptions of the individual molecules from the absorption of the mixture, C = as B, but due to smaller changes between the absorptions of the individual molecules and the composite system less accurate.

Kinetic Measurements

The Benesi-Hildebrand procedure to obtain equilibrium constants for CT-complex formation[2] can not be applied to transient charge-transfer complexes. These constants can, however, be determined from the measurement of reaction rates and an analysis of the rate data in terms of eq. (3) and (4) which derive from eq. (1) and (2), respectively. This procedure was first applied to the Diels-Alder reaction by Andrews and Keefer[5].

$$k_2' = \frac{k_1'[\mathrm{D}]}{1 + K[\mathrm{D}]} \tag{3}$$

$$k_2 = \frac{k_1}{1 + K[\mathrm{D}]} \tag{4}$$

A determination of k_2 resp. k_2' as a function of the diene (D) concentration allows the determination of the equilibrium constant for complex formation and the rate constants k_1 and k_1'.

Measurements were carried out for the reaction of **1** with dienophiles **2**–**5** in methylene chloride at 20 °C with a 4 to 250-fold excess of the diene. From the pseudo-first-order rate constants we calculated the second-order rate constants. A plot of $1/k_2$ (eq. 4) versus the diene concentration yields the equilibrium constants K and the rate constants k_1.

Table 3. Second-order rate constants for the reaction of 2,3-bis(methylene)norbornane (**1**) with dienophiles **2**–**4** and equilibrium constants for CT-complex formation, evaluation according to eq. (3) ($c_{dienophile} = 1.0 \times 10^{-4}$ M, solvent methylene chloride, 20 °C)

Dienophile	c_{diene} (mol/l · 10^2)	$1/k_2$ (s · mol/l)	K (l/mol)
2	0.473	29.7 ± 1.0	3.8 ± 1.4
	0.506	29.8 ± 0.5	
	1.01	30.4 ± 0.9	
	1.26	30.6 ± 0.7	
3	0.206	0.301 ± 0.009	33.5 ± 0.1
	0.515	0.332 ± 0.009	
	1.03	0.380 ± 0.007	
	1.13	0.388 ± 0.011	
4	0.081	0.253 ± 0.0080	79.1 ± 1.7
	0.202	0.261 ± 0.0004	
	0.404	0.297 ± 0.0009	
	0.505	0.317 ± 0.0010	
	0.509	0.314 ± 0.0010	

Table 3 displays the relevant kinetic data for the dienophiles **2**–**4** and the equilibrium constants for CT-complex formation. Because of the high reactivity of **5** towards **1** we were not able to determine an equilibrium constant for complex formation under analogous experimental conditions.

According to the equilibrium constants, all being > 1, the equilibrium lies on the side of the CT complexes and the following free energies of formation for the CT complexes at 300 K are calculated: 2,3-dicyano-*p*-benzoquinone (**2**) and **1** −0.80 kcal/mol, tetracyanoethylene (**3**) and **1** −2.08 kcal/mol and 2,3-dicyanomaleimide (**4**) and **1** −2.60 kcal/mol.

The order of reactivity of the dienophiles **2**–**5** was evaluated from independent kinetic experiments where the data were analysed on the basis of the usual assumption that the Diels-Alder reaction is second order, not taking account of possible CT-complex formation. The values are thus effective second-order rate constants and can be compared with values in the literature. In Table 4 absolute and relative rate constants, measured either in methylene chloride or in dioxane at 20°C, are reported. The order of reactivity corresponds to that for the reactions of the same dienophiles with other dienes[23] (2,3-dimethyl-1,3-butadiene, isoprene, and anthracene). In methylene chloride there is a factor of ca. 900 between the least reactive dienophile 2,3-dicyano-*p*-benzoquinone and the most active dienophile *p*-benzoquinone-2,3-dicarboxylic anhydride. This range is smaller in dioxane, however, the relative order remains the same.

Table 4. Second-order rate constants (l/mol · s) and relative rate constants for the cyloaddition of 2,3-bis(methylene)norbornane (**1**) with dienophiles **2**–**5** at 20°C

Dienophile	k_2[a)]	k_{rel}[a)]	k_2[b)]	k_{rel}[b)]
2	0.0349	= 1.0	0.003	= 1
3	2.81	81	0.168	56
4	3.18	91	0.239	80
5	32.0	917	0.838	279

Solvents: [a)] methylene chloride and [b)] dioxane.

Electron Affinities of the Dienophiles 2–5

A discussion of reactivity phenomena in terms of frontier molecular orbital (FMO) theory requires to know the energies of both the highest occupied and the lowest unoccupied molecular orbitals. The cycloadditions of **1** to dienophiles **2**–**5** are HOMO$_{\text{diene}}$-LUMO$_{\text{dienophile}}$ controlled. A good experimental approximation to the LUMO energies are the electron affinities (E_a) of the dienophiles. In Table 5 we have collected the $E_{1/2}^{\text{red}}$ values vs. SCE, measured in acetonitrile, where we used a positive sign for $E_{1/2}^{\text{red}}$ of strong acceptors[24]. The value of 0.25 V for tetracyanoethylene reproduces the 0.24 V in ref.[25] very well. The electron affinities were calculated on the basis of eq. (5)[26].

$$E_a(\text{eV}) = E_{1/2}^{\text{red}} + 2.49 \pm 0.26 \qquad (5)$$

In using a positive sign for $E_{1/2}^{\text{red}}$ in eq. (5) we followed the convention of Peover[24] and not that of ref.[26] and others[27] who use a negative sign for strong acceptors.

Table 5. $E_{1/2}^{\text{red}}$ (V) vs. SCE and E_a (V) of the dienophiles **2**–**5**

Dienophile	$E_{1/2}^{\text{red}}$ (V)	E_a (eV)
2	0.320	2.81
3	0.250	2.74
4	0.025	2.52
5	0.455	2.95

Discussion

Reactivity in the area of cycloaddition chemistry has been explained successfully on the basis of frontier molecular orbital theory[28,29]. In a more sophisticated form configuration interaction treatments have been used[16,30,31]. Both models attribute great significance to charge-transfer interactions as forces which stabilise the transition state of these reactions and which are the primary reason for the formation of new bonds. The present study was initiated to elucidate the significance of charge-transfer complexes in this context.

The cycloadditions of 2,3-bis(methylene)norbornane (**1**) to the dienophiles **2**–**5** are HOMO$_{\text{diene}}$-LUMO$_{\text{dienophile}}$ controlled. Figure 4 represents the experimental values for HOMO$_{\text{diene}}$, taken from its photoelectron spectrum[32], and the LUMOs of the dienophiles which correspond to their electron affinities in eV. As the reactivity depends in FMO theory on $1/(E_{\text{HOMO}}\text{-}E_{\text{LUMO}})$ we would expect **5** to be the most reactive dienophile and 2,3-dicyanomaleimide to be the least reactive. The same conclusion has to be drawn from the charge-transfer excitation energies which can be calculated from the wavelengths of the CT absorptions. In THF these energies are: $h\nu_{\text{CT}}$ ($\mathbf{1}\rightarrow\mathbf{2}$) = 2.70–2.76 eV, $h\nu_{\text{CT}}$ ($\mathbf{1}\rightarrow\mathbf{3}$) = 2.90 eV, $h\nu_{\text{CT}}$ ($\mathbf{1}\rightarrow\mathbf{4}$) = 2.95 eV, and $h\nu_{\text{CT}}$ ($\mathbf{1}\rightarrow\mathbf{5}$) = 2.58–2.76 eV. This result is expected because the required energy for exciting an electron from the HOMO of the diene into the LUMO of the dienophile should be proportional to the HOMO-LUMO gap. The value of $h\nu_{\text{CT}}$ is smaller than the corresponding $\Delta E_{\text{HOMO-LUMO}}$ because the CT-excitation energy includes the coulombic interactions between the donor and acceptor. The resemblance of the excited CT complex with an ion pair has been demonstrated by the elegant studies of Kochi and Rentzepis[33].

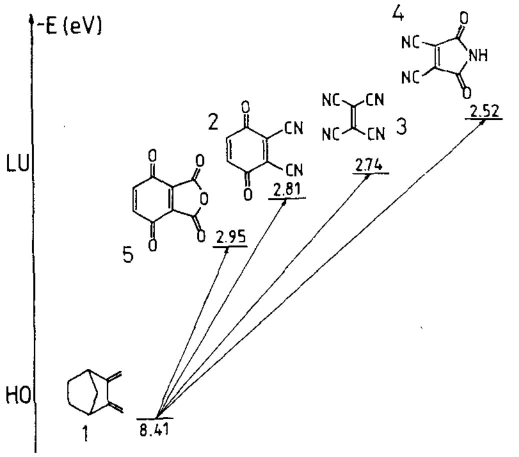

Figure 4. HOMO (**1**) and LUMOs (**2**–**5**) in eV

The comparison of the HOMO-LUMO separations and the relative rates, however, reveals differences between our expectation from the simple reactivity model and the experimental results. Especially, 2,3-dicyano-*p*-benzoquinone (**2**) deviates. It should be second in reactivity on the basis of its electron affinity and the observed CT-excitation energy but it is found to be the least reactive. In other cases, i.e. the cycloadditions of substituted anthracenes and tetracyanoethylene, Kochi and Fukuzumi[11,12] reported a perfect correlation between the logarithms of the rate constants and $h\nu_{\text{CT}}$. This may be due to the relative small changes in the molecular structure of the dienes in the series. In our case there is less structural similarity between the dienophiles and other effects, neglected so far, might become apparent. This demonstrates that in the case of substituted anthracenes the correlation may be accidental.

If $h\nu_{CT}$ is calculated theoretically a transition moment operator and not a Hamiltonian operator is applied to the wave function. It, therefore, does not constitute an interaction energy. The correlation of reactivity with $1/(E_{HOMO} - E_{LUMO})$ represents the simplest possible reactivity model[30]. In order to calculate frontier molecular orbital interaction energies properly not only the energies of the relevant frontier orbitals have to be considered but also their shapes. The shape is obtained from the eigenvector coefficients and they enter the expression of the FMO stabilisation in the numerator. As will be shown in the accompanying publication[19] a reconciliation of theory and experiment can be achieved by explicitly taking into account the shape of the frontier molecular orbitals.

There is, however, another interesting observation made in our study. For three of the four dienophiles we determined equilibrium constants for CT-complex formation. The comparison of these values with the relative reactivities reveals an increasing rate with increasing equilibrium constants. Does this indicate and require that the CT complex is part of the experimental reaction coordinate? The greater the equilibrium constant is the more stable is the CT complex. On the basis of Mulliken's theory the equilibrium constant indicates stabilisation of the ground state of the CT complex by charge-transfer interactions, i. e. the stronger the complex is the more important is the charge-transfer stabilisation energy. This stabilisation energy is, on the other hand, also the most important contribution to the stabilisation of the transition state of the cycloaddition according to perturbation theory[15,28,29]. From this point of view the correlation of equilibrium constants with rates of reaction is not unexpected. The correlation of the logarithms of the relative rates with the logarithms of the relative stability of the CT complexes discloses another interesting feature. Even though there are only three points and, therefore, the conclusions can be at most semiquantitative, the slope of this linear-free-energy plot is indicative of the importance of CT interactions in the ground state of the CT complexes and in the transition state of the cycloadditions. The results is that CT interactions in the transition states are more important by a factor of three to four. A factor greater one is indeed expected from theoretical considerations. CT interactions are proportional to the square of the resonance intergrals between the orbitals involved. These are proportional to the overlap integrals and they increase exponentially with decreasing distance. It seems to be sure to assume that the separation of the donor and acceptor molecule in the ground state of the CT complex is greater than in the transition state.

Does this discussion shed some light on the intermediacy of CT complexes in cycloadditions? As stated in the introduction CT complexes are of kinetic relevance if the complex formation is rate determining. This was the case in the study of Kiselev and Miller[9]. In all other cases where positive $\Delta H^{\neq}$ values are observed the question can not be answered. However, we can conclude that the interactions which lead to the formation of CT complexes are also important in the transition state. The theoretical model does not require the CT complex to be an intermediate. The transition state can take advantage of the CT interactions without prior formation of the CT complex. Therefore, the importance which is attributed in some cases to CT-complex formation should be shifted to a consideration of the CT interactions in the transition state.

A final remark on the so-called electron-transfer activation of the Diels-Alder reactions seems to be necessary[11,12]. As long as this is not interpreted as a complete transfer of an electron from the donor to the acceptor in the transition state concomittant with the formation of a radical ion pair it is in line with the interpretation given here. Electron-transfer into the region where new bonds are being formed is necessary and is described theoretically by CT interactions. A complete transfer of an electron from a donor diene to an acceptor dienophile has been observed experimentally[14] and its relevance for [4 + 2] cycloadditions has been discussed and is still under investigation[34].

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Experimental

Analytical instruments: ^{1}H- and ^{13}C-NMR spectra (internal standard TMS): Varian XL 200 and EM 360 A. – Mass spectra: Finnigan MAT 312/188. – IR spectra: Perkin Elmer 397. – UV spectra: Varian Cary 219. – Melting points are uncorrected.

Starting materials: 2,3-Bis(methylene)norbornane (**1**)[35], 2,3-dicyano-*p*-benzoquinone (**2**)[36,37], 2,3-dicyanomaleimide (**4**)[38], *p*-benzoquinone-2,3-dicarboxylic anhydride (**5**)[39]. Commercial tetracyanoethylene (**3**) was purified by repeated sublimation under reduced pressure and stored under argon.

Cycloadducts **6**–**8**: The same procedure was followed in all cases. The diene and the dienophile, in the molar amounts of Table 6, were dissolved in half of the total solvent and treated after mixing under the indicated conditions at room temperature. After removing the solvent in vacuo the 60 MHz ^{1}H-NMR spectra of the crude mixtures revealed no other products than the expected cycloadducts and were essentially identical with those of the recrystallized material. Recrystallisation afforded one of the stereoisomers in enriched form. Table 7 collects some spectroscopic data of the recrystallized cycloadducts.

CT Complexes: The measurements were carried out at −90°C in a quartz Dewar vessel with a builtin UV cell according to Figure 5. The temperature of the UV cell was controlled by a stream of precooled nitrogen. The temperature of the nitrogen stream was regulated by a temperature unit similar to those used in NMR spectrometers. This unit allows the temperature to be regulated between −110 and ±65°C. Above −60°C the temperature is constant within 0.2°C, at lower temperatures the variation is 2°C. Within the cell itself the temperature gradient is 0.2°C.

The measurements are described for the CT complex of **1** with **4**: 2.0 ml of a 0.1 M solution of **4** in THF is cooled in the 1.0 cm UV cell to −90 to −100°C in the UV spectrometer. Its absorption spectrum was recorded showing the beginning of absorptions at this concentration at λ = 500 nm. 2.0 ml of a 0.1 M solution of **1** in THF was kept in an argon-purged syringe to which a long needle

Table 6. Cycloaddition conditions for **1** with **2**, **4**, and **5**

Dienophile mmol	**1** mmol	Solvent Reaction time	Yield (%)	M.p. °C	Empirical formula Mol. weight	Analysis Calcd. (Found) C	H	N
2 1.67	1.67	30 ml CH_2Cl_2 3 d	75 (*n*-propanol)[a]	170[b] 191[b]	$C_{17}H_{14}N_2O_2$ 278	73.36 (73.54)	5.08 (5.08)	10.07 (10.01)
4 3.3	3.3	20 ml dioxane 20 h	60 (ethanol)[a]	198[b] 232[b]	$C_{15}H_{13}N_3O_2$ 267	67.39 (67.08)	4.91 (4.91)	15.72 (15.55)
5 3.6	3.6	35 ml CH_2Cl_2 (suspension) 24 h	65 (benzene/ cyclohexane)[a]	98[b] 132[b]	$C_{17}H_{14}O_5$ 298	68.44 69.19	4.74 4.67	– –

[a] Solvent for recrystallisation. — [b] Mixtures of stereoisomers of different composition.

Table 7. Spectroscopic data for cycloadducts **6**–**8**

	MS (110 eV): *m*/*z* (% rel. Int.)	IR (cm^{-1})	UV (solv.)	$\lambda_{max}/\varepsilon$ (nm)
6	278 (M^+, 41.1), 250 (100.0), 233 (38.9), 222 (72.4), 221 (31.3), 194 (40.3), 167 (24.6), 160 (23.3), 132 (11.1), 105 (9.1), 91 (58.8)	3060 (s, $\nu_{=C-H}$), 2960, 2870 (s, ν_{C-H}), 2260 (w, $\nu_{C\equiv N}$), 1710 (s, $\nu_{C=O}$), 1600 (m, $\nu_{C=C}$)	(CH_2Cl_2) (Dioxan)	234/12200 233/9280
7	268 (0.65), 267 (M^+, 6.3), 240 (6.5), 239 (39.1), 212 (6.5), 196 (2.8), 168 (8.7), 141 (9.8), 105 (4.8), 92 (79.3), 91 (100.0), 78 (39.1), 77 (6.5), 52 (5.4)	3190 (s, ν_{N-H}), 2950, 2880 (s, ν_{C-H}), 2250 (m, $\nu_{C\equiv N}$), 1725 (s, $\nu_{C=O}$), 1435 (m, ν_{C-H})	(CH_2Cl_2) (Dioxan)	248/602 245/492[a]
8	298 (M^+, 19.4), 270 (2.4), 252 (39.8), 226 (51.0), 198 (100.0), 169 (22.3), 141 (16.0), 115 (46.6), 91 (10.0), 82 (19.4), 54 (20.4), 39 (14.6)	2950, 2860 (m, ν_{C-H}), 1790, 1770 (w, $\nu_{C=O}$), 1685 (w, $\nu_{C=C}$), 1150 (w, ν_{C-O})	(CH_2Cl_2) (Dioxan)	319/1050 289/1630 263/1430[a] 320/1020[a] 292/1710 220/9060

[a] Shoulder.

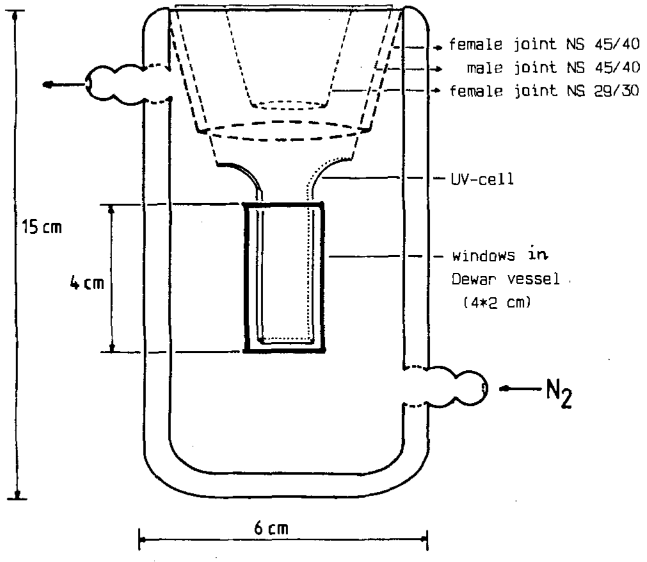

Figure 5. Quartz UV cell for low temperature measurements

reaching the bottom of the UV cell could be attached. The syringe was sealed with a rubber stopper and cooled for 3 min in liquid nitrogen so that the solution did not freeze. Afterwards the rubber stopper was replaced by the needle and the solution was introduced through a septum rapidly in order to achieve good mixing with the precooled solution of **4**. In this way the temperature of the combined solutions, checked by a thermoelement, did not change by more than 2°C. Then the spectrum was recorded immediately. The increased absorption was determined after correcting for the absorption of the dienophile. The diene does not show absorptions in the region where the increase is observed. Already after 5 min the additional absorption decreased and disappeared. Table 2 reports the results of these measurements.

Electron Affinities: The measurements were carried out with a Bruker polarograph model E 310. Solvent: acetonitrile, electrolyte: tetrabutylammonium tetrafluoroborate (0.1 M), saturated calomel electrode as reference, concentration of the dienophile 0.01 M.

Kinetic Measurements: All measurements were done UV spectrophotometrically at 20°C using either the UV cell described in Figure 5 for direct measurements or externally thermostatised vessels from which probes were taken, diluted, and their extinctions measured. The stability of the compounds in methylene chloride and dioxane was secured prior to the measurements. At least 10, normally 20–25 points were used for the kinetic evaluation. Kinetics were followed to ≥ 80% turnover and individual measurements were repeated six times. For further details see ref.[40].

In Table 8 the data of the kinetic measurements are collected which were obtained using a second-order rate expression for the cycloadditions. Table 9 lists the results for the measurements in which pseudo-first-order rate constants were determined as function of the diene concentration (4–250-fold excess) in order to calculate equilibrium constants for CT-complex formation.

Table 8. Second-order kinetics of the reaction of **1** with dienophiles **2**−**5** in A) methylene chloride and B) dioxane

Dieno-phile	$\bar{c}_0$ (M)	λ (nm) ε (diene) ε (dienophile) ε (adduct)	$\bar{k}_2$ (l mol^{-1} s^{-1})
2	A) $2.35 \cdot 10^{-2}$	264.4 4640 14800 536	$3.49 \cdot 10^{-2} \pm 0.10 \cdot 10^{-2}$
	B) $7.95 \cdot 10^{-2}$	259.1 6720 15200 985	$3.00 \cdot 10^{-3} \pm 0.08 \cdot 10^{-3}$
3	A) $1.18 \cdot 10^{-3}$	266.4 2920 14800 0	2.81 ± 0.08
	B) $1.04 \cdot 10^{-2}$	258.8 6390 13900 0	0.168 ± 0.005 (Lit.[41] 0.161)
4	A) $2.74 \cdot 10^{-4}$	253.5 10100 15600 562	3.18 ± 0.1
	B) $5.31 \cdot 10^{-3}$	247.8 9800 13600 456	0.239 ± 0.007
5	A) $2.01 \cdot 10^{-4}$	252.4 9740 11500 2460	32.0 ± 0.7
	B) $1.01 \cdot 10^{-3}$	247.0 9850 12100 3630	0.838 ± 0.03

Table 9. Pseudo-first-order kinetics of the reaction of **1** with **2**−**4** in CH_2Cl_2 at 20°C [c (dienophile) = 1.0×10^{-4} M]

Dieno-phile	c_{diene} (mol/l × 10^2)	λ ε (diene) ε (dienophile) ε (adduct)	$\bar{k}_1$ (l s^{-1} × 10^2)	k_2 (l mol^{-1} s^{-1})
2	0.473	280	1.59 ± 0.05	3.37 ± 0.11
	0.506	16	1.70 ± 0.03	3.36 ± 0.16
	1.04	8640	3.32 ± 0.10	3.29 ± 0.10
	1.26	0	4.12 ± 0.09	3.27 ± 0.07
3	0.808	280	0.320 ± 0.01	3.96 ± 0.12
	2.02	16	0.774 ± 0.02	3.83 ± 0.01
	4.04	821	1.36 ± 0.04	3.37 ± 0.01
	5.05	0	1.59 ± 0.05	3.15 ± 0.01
	5.09		1.62 ± 0.05	3.18 ± 0.01
4	0.206	280	0.684 ± 0.02	3.32 ± 0.10
	0.515	16	1.55 ± 0.04	3.01 ± 0.08
	1.03	11900	2.71 ± 0.05	2.63 ± 0.05
	1.13	0	2.92 ± 0.08	2.58 ± 0.07

CAS Registry Numbers

1: 36439-78-8 / **1** · **2** (CT complex): 108148-11-4 / **1** · **3** (CT complex): 108120-80-5 / **1** · **4** (CT complex): 108120-81-6 / **2**: 4622-04-2 / **3**: 670-54-2 / **4**: 1974-53-4 / **5**: 63401-20-7 / **6A**: 108211-42-3 / **6B**: 108120-77-0 / **7A**: 108120-78-1 / **7B**: 108210-95-3 / **8A**: 108120-79-2 / **8B**: 108210-96-4

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