284. Physical and Chemical Interaction
## of Homoconjugated Dienes with Tetracyanoethylene[1])

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Summary. EDA-complexes of bicyclo[2,2,n]alkadienes (n = 1, 2, 3, 4) (**1** (n)-series), 1,4-cyclo-hexadiene (**2**) and various other cyclic monoenes, dienes and trienes as donors and tetracyano-ethylene (TCNE) as acceptor were investigated. Spectroscopic and thermodynamic constants of the complexes were determined and correlated with the ionisation potentials (I^D) of the hydro-carbon donors obtained from PE. spectroscopy. The nature of the dominant energy contributions to the ground state and the two lowest CT-states of these weak complexes is discussed and struc-tural conclusions are drawn. The role of the complexes in the addition reaction of the hydrocarbon components and TCNE is discussed. The *homo Diels-Alder* addition product of **1** (2) and TCNE, 9,9,10,10-tetracyanoquadricyclo[2,2,2,0²,⁶,2³,⁵]decane, and the 'ene'-addition product of **2** and TCNE, 5-[1′,1′,2′,2′-tetracyanoethyl]-1,3-cyclohexadiene were prepared and characterized. Preliminary results for the mechanistic scheme governing the dehydrogenation of **2** by TCNE are reported.

Introduction. – *Heilbronner et al.* have conclusively shown that for the series of homoconjugated dienes **1** (n) (n = 1, 2, 3, 4) and **2** the ground electronic state of their radical cations changes from $^2B_2$- for small n to $^2A_1$-symmetry for large n or for **2** [2].

1(n), n=1,2,3,4   2   3   4   5

6   7   8   9   10
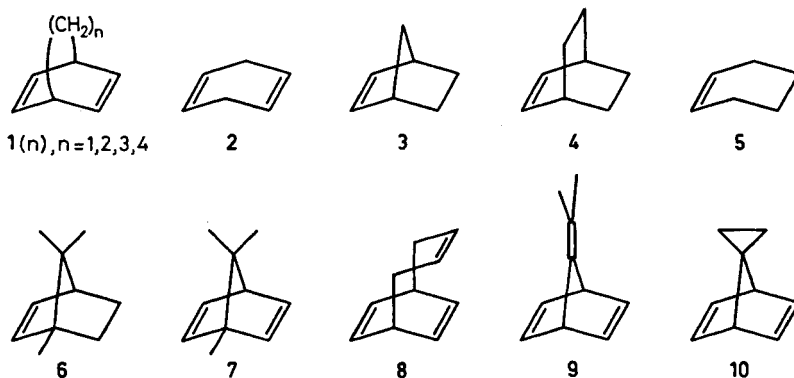
Assuming *Koopmans'* theorem to be valid the orbital scheme of Fig. 1 holds for the two highest occupied MO's. We decided to examine the CT-spectra of these donor systems (D) using TCNE as acceptor (A) with the idea in mind that the above feature might manifest itself in the intensity ratio of the two low energy CT-transi-

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[1])   Part 3 of the series: 'Weak molecular complexes with hydrocarbon donors'. Part 2: [1].
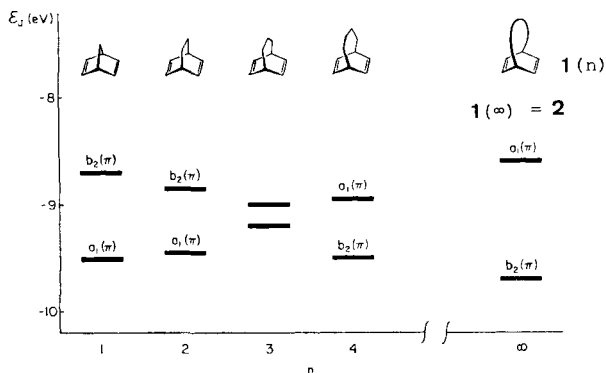
Fig. 1. *Orbital scheme for the two highest occupied orbitals of the homo-conjugated dienes* **1** (n) (n = 1 to 4) *and* **2**, *deduced from PE-spectroscopy* [2]

tions expected in these systems. Furthermore, since weak EDA-complexes with non-aromatic D's of the present kind are virtually unmentioned in the literature, it was of interest to examine their stabilities and to relate them to properties of the D's such as the first ionization potential (I_1^D), the chemical reactivity *etc*. In order to shed light on the role of homoconjugation in these systems, several complexes involving monoenes as donors were studied as reference systems. For the sake of completeness data for the systems **8**, **9** and **10** are also reported, but shall not be further discussed.

Results. – *Measurement of spectra.* The measurements, carried out at 25° in CH$_2$Cl$_2$-solution[2]), were subjected to a *Benesi-Hildebrand* treatment using a least squares computerized procedure. For **1** (1), **1** (2), **2** and **7**, where under these conditions reaction with A took place, the optical densities were extrapolated to t = 0.

Experience indicates that the mean error of the extinction coefficient ε is much larger than that of the product $^xK\varepsilon$, ^xK being the equilibrium constant of (1)

$$D + A \underset{\longleftarrow}{\overset{^xK}{\rightleftharpoons}} DA \qquad (1)$$

in mole fraction units. If the error of $^xK\varepsilon$ is neglected, then the standard error of ^xK is directly related to that of ε. The measured values and their standard errors are quoted in Tab. 1, together with the ν_{max}-values of the CT-transition (s).

Recent work on other EDA-complexes [3] suggests that the ^xK- as well as the ΔG^0-values of Tab. 1 are only apparent ones ($^xK_{ap}$, ΔG^0_{ap}) since the observed equilibria involve in addition to DA-complexes (*cf.* eq. (1)) also termolecular complexes D$_2$A as well as complexes between A and the solvent. The presence of D$_2$A-complexes does not greatly affect the thermodynamic parameters (*cf.* [3] [4]), in contrast to the solvent competition problem, which necessitates appreciable correction terms [5]. These are presumably rather constant for a given A in a given solvent [1]. Using the

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[2]) For the complexes of **1** (1), **2** and **3** measurements were carried out at various temperatures.

Table 1. *Spectral and thermodynamic data for the EDA-complexes* (for symbols see text)

	$\tilde{\nu}^{CT}$ (cm^{-1})	ε (l mol^{-1} cm^{-1})[c]	$(^xK\varepsilon \pm s)^{-1}$[c]	$^xK_{ap}$	ΔG^0_{ap} (kcal mol^{-1})[d]	ΔG^0_1 (kcal mol^{-1})[d]	ΔH^0_1 (kcal mol^{-1})[d] ΔS^0_1 (e.u.)
1 (1)	21 400	590 (540–650)	$(8.58 \pm 0.08) \times 10^{-4}$	1.97 (1.79–2.14)	1.22	−0.43	− 3.70 −11.00
1 (2)	23 500	890 (720–1180)	$(3.8 \pm 0.2) \times 10^{-4}$	2.94 (2.23–3.65)	0.99	−0.66	
1 (3)	23 800	260 (230–300)	$(1.9 \pm 0.05) \times 10^{-4}$	20.42 (17.63–23.21)	−0.16	−1.81	
1 (4)	25 200	~200	~4.28×10^{-4}	11.69	0.17	−1.48	
2	22 500 28 600	2150 (2050–2270) 1740 (1650–1830)	$(5.09 \pm 0.35) \times 10^{-4}$	0.91 (0.85–0.98)	1.68	0.03	− 3.22 −10.93
3[a]	23 700	445 (340–635)	$(1.35 \pm 0.09) \times 10^{-3}$	1.67	1.32	−0.33	− 2.82 − 8.46
4	24 300	260 (163–610)	$(2.01 \pm 0.06) \times 10^{-3}$	1.93 (0.81–3.04)	1.23	−0.42	
5	24 500	2000 (1370–3700)	$(1.11 \pm 0.03) \times 10^{-3}$	0.45 (0.24–0.65)	2.09	0.44	
6	23 500	680	3.06×10^{-3}	0.48	2.05	0.40	
7[b]	19 500 26 500	500	6.55×10^{-4}	3.06	0.96	−0.69	
8	24 100	220	1.71×10^{-4}	26.53	−0.31	−1.96	

[a]) Data for T = 296 K.
[b]) Data for T = 273 K.
[c]) s = Standard deviation of the slope of the *B–H* plot.
[d]) Values based on ^eK-equilibrium constants; $^eK = {}^xK \times 0.0636$ l · mol^{-1} for CH$_2$Cl$_2$.

correction equation derived in [1] we arrive at the estimates for the free energies of formation ΔG_1^0 for the (1:1)-complexes quoted in Tab. 1. Equally, ΔH_1^0 and ΔS_1^0 follow on the basis of [1] for those complexes, where the temperature dependence of the equilibrium has been studied.

Deconvolution of spectra. Only the spectra of the complexed dienes **1** (1) and **2** do clearly indicate the presence of two CT-transitions, in line with the fact that these two donors also have the largest gap between I_1^D and I_2^D (Tab. 2). For the other

Table 2. *Ionisation potentials of the donors; position of band maxima of the deconvoluted CT-bands*

	$I_1^{D\ a)}$	$I_2^{D\ a)}$ (eV)	$\tilde{\nu}_1^{CT}$ (cm^{-1})	$\tilde{\nu}_2^{CT}$ (cm^{-1})	$\varepsilon_1^{CT}/\varepsilon_2^{CT}$	ΔI^D (eV)	$\Delta\tilde{\nu}^{CT}$ (eV)
1 (1)	8.70	9.55	21400 ± 300	27800 ± 300	1.95	0.85	0.79 ± 0.07
1 (2)	8.85	9.45	22700 ± 300	26600 ± 300	2.19	0.60	0.48 ± 0.07
1 (3)	9.00	9.20	22900 ± 300	24900 ± 300	1.48	0.20	0.24 ± 0.07
1 (4)	8.95	9.30	22600 ± 300	25700 ± 300	.89	0.35	0.38 ± 0.07
2	8.80	9.80	22300 ± 300	28700 ± 300	1.13	1.00	0.79 ± 0.07
3	8.97		23700				
4	9.05		24300				
5	9.12		24400				
6	8.76[b)]		23500				
7	8.42[b)]	9.34[b)]	19500 ± 300	26500 ± 500	~ 8	0.92	0.87 ± 0.1
8	8.88[b)]	9.44[b)]	23550 ± 300	28200 ± 300	2.39	0.56	0.57 ± 0.07
9	7.97	9.25	17300	26500 ± 500	1.38	1.28	1.14 ± 0.06
10	8.37	9.26	20400	27300 ± 500	1.32	0.89	0.85 ± 0.06

[a)]   Vertical ionisation potentials from [6].
[b)]   Unpublished values.

systems the deconvolution technique described in [1] was used. The parameters responsible for the shape of the two *Gaussians* were at first calibrated with the well resolved bands of **2**A. Application to the other spectra led with a 'trial and error' process to the optimal set (*cf.* [1]):

$$B = 0.15 \ , \ D = 5800 \text{ cm}^{-1} \text{ for first } \quad CT\text{-band}$$
$$B = 0.235, \ D = 5800 \text{ cm}^{-1} \text{ for second } CT\text{-band} \tag{2}$$

The resolved band maxima as well as their intensity ratio are given in Tab. 2. The spectra are displayed in Fig. 2.

Temperature dependence of CT-spectra. Extinction coefficients of CT-bands of stable molecular complexes have been found to be more or less T-independent [7]. For such systems the absorbance at any λ increases by a constant factor for a T-decrease ΔT, due to an increase in the association constant. It follows that the ratio of absorbances of any two bands is independent of T.

In Fig. 3 the CT-spectra of some complexes, taken in fluid and glassy medium, are displayed. Obviously, the above said is not valid for the present substrates. The monoenes exhibit a drastic blue shift of the band maxima on cooling. The diene band positions are not greatly affected, but the intensity ratio between long and short
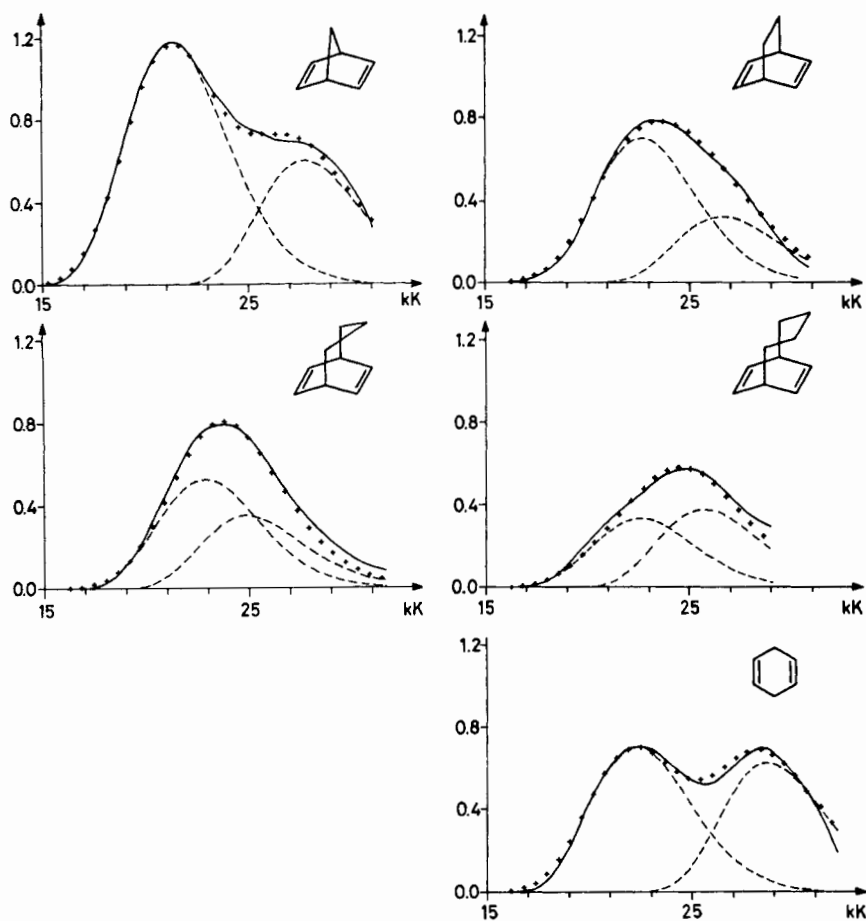
Fig. 2. *Experimental* (−), *deconvoluted* (− −) *and synthesized* (+ +) *CT-spectra of the homoconjugated dienes with TCNE*

wavelength transitions has decreased. Phenomenologically it appears as if the spectra arise from the superimposed absorptions of a distribution of different species. On cooling, the concentration of those contributing mainly to the long wavelength absorption decreases. On an absolute scale, the absorbance for the dienes increases at any λ, whereas the long wavelength absorbance for the monoenes in fact decreases[3]).

Experience from earlier work suggests that the above features are due to the presence of contact CT-complexes, whose formal concentration on T-lowering decreases in favor of that of the stable complex [7]. It is reasonable to find contact complexes to be important for the present D/A-couples, in particular for the monoenes, given their weak nature (*cf.* Tab. 1). To our knowledge the latter systems provide the first example where T-lowering results in a decrease of total CT-absor-

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[3])   This feature is not evident from Fig. 3 as the concentrations of D were chosen differently for the two T-ranges; *i.e.* lower [D] for lower T.
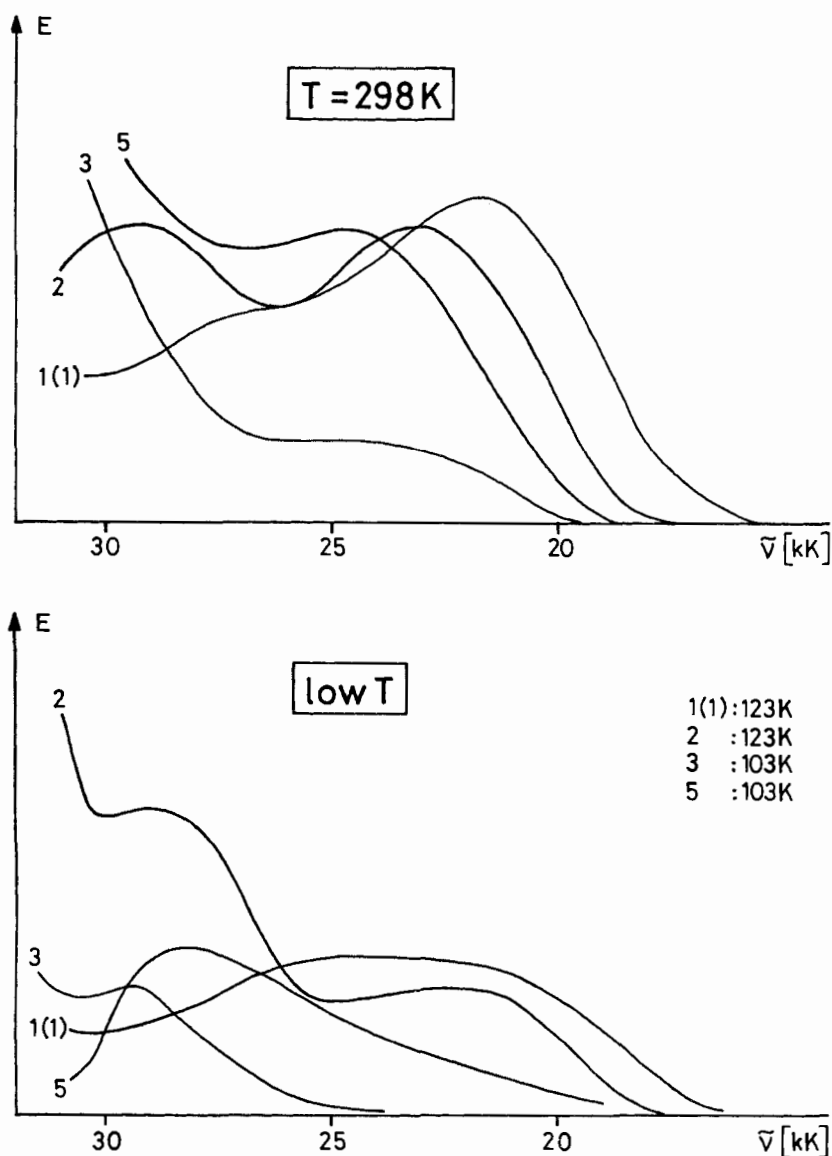
Fig. 3. *CT-spectra in fluid and glassy* (*n*-BuCl/CH₂Cl₂, 3:2 by vol.) *medium.* (Arbitrary concentrations of D, [TCNE] $= 6.43 \times 10^{-3}$ м)

bance (for the low energy region of the spectrum), indicating dominant contact CT-contributions. We can not, however, exclude that the intrinsic CT-transition energy of the stable complex is also not subject to changes due to matrix effects.

As a final point for the presence of contact CT-interaction we note from Tab. 1 that the ε-values roughly increase with decreasing complex stability (for a discussion of this criterion see [7] [8]). We note in particular the high ε-values for **2**A and **5**A

which are the weakest complexes of the series and therefore most subject to contact CT-interaction.

Discussion. – 1. *Correlation between ionization potentials and CT-excitation energies.* According to the theory of weak molecular complexes the relationship between I^D and $h\nu^{CT}$ is given by

$$h\nu^{CT} = I^D - C_1 + C_2 (I^D - C_1)^{-1} \tag{3}$$

with C_1, C_2 being positive constants. For a limited range of I^D-values the parabolic equation (3) can be approximated by the linear one (4)

$$h\nu^{CT} = aI^D - b \tag{4}$$

It is evident that the smaller C_2 is in eq. (3) the more will a in (4) approach unity (a = 1). C_2 increases with increasing CT-interaction in the ground state of the complex [9]. Hence the closer a is to unity, the smaller is this interaction.

For the present olefinic D's (mono- and dienes) the constants in (4) are (in eV)

$$a = 0.911 \pm 0.049, \; b = 5.275 \pm 0.448 \tag{5a}$$

From the solution data given in [1] the corresponding values for the alkylbenzene-TCNE complexes are (in eV):

$$a = 0.768 \pm 0.041, \; b = 3.812 \pm 0.353 \tag{5b}$$

Both correlations are shown in Fig. 4; their quality incidentally supports the deconvolution technique used and described in [1]. The standard conclusion here is that
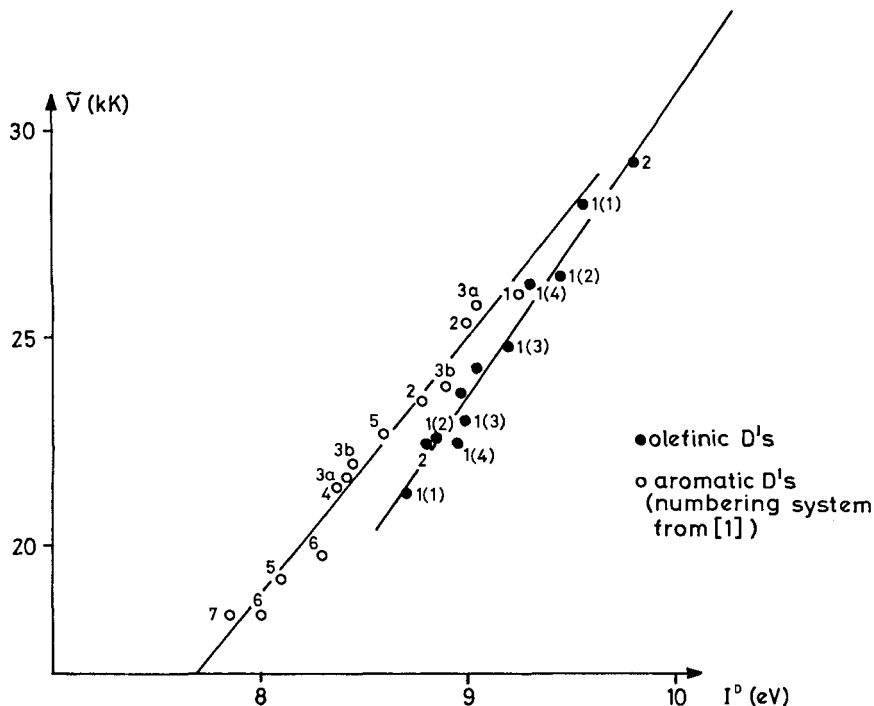

Fig. 4. *Plot of $h\nu^{CT}$ vs. I^D for olefinic and aromatic donors* (A = TCNE)

CT-interaction for the olefinic D's is very small, at any rate smaller than that for the aromatic D's where a is significantly different from unity. However, this outcome is rather surprising since both sets of complexes:

– involve pure hydrocarbon donors, equal acceptor and equal solvent,
– are of π–π sacrificial type,
– exhibit rather similar ionization potentials and CT-energies, suggesting comparable interactions between no-bond and dative configurations.

A modification of eq. (4) indicates a way out of this problem. It has since long been recognized [10], and is supported by recent high quality quantum chemical calculations [11], that the dominant contribution to the ground state stabilization of complexes of this type is the dispersion energy (E_{disp}) between D and A. Hence, a < 1 in (4) might in fact indicate strong E_{disp}-variations in the series of complexes. If this were the case then a' in (6)

$$h\nu^{CT} - \Delta H_1^0 = a' I^D - b' \qquad (6)$$

or, assuming a roughly constant entropy term for the series, a'' in (7)

$$h\nu^{CT} - \Delta G_1^0 = a'' I^D - b'' \qquad (7)$$

should be nearer unity than a of eq. (5). Application of eq. (7) to the present complexes yields (in eV):

$$a'' = 0.919 \pm 0.066, \; b'' = 5.377 \pm 0.604 \qquad (8a)$$

which is similar to eq. (5a), in line with the small differences in the thermodynamic parameters of Tab. 1. On the other hand we obtain from the ΔH_1^0-data in [1] for the aromatic substrates (in eV):

$$a' = 0.883 \pm 0.051, \; b' = 5.057 \pm 0.433 \qquad (8b)$$

i.e. a significant increase of the slope with respect to eq. (5b), which reflects the much larger variations in the complex stabilities within this series. This is also reasonable given that the benzenes have clearly higher polarizabilities (α) than the present olefins. Hence, variations in α on replacement of H for alkyl groups are also expected to be larger in the case of the aromatics.

2. *Correlation between complex stability and I_1^D*. Numerous correlations of the above type have generally shown an increase in complex stability (as measured e.g. by ΔG_1^0) with decreasing I_1^D of the donor [7]. This – also true for the benzene series in [1] – led many authors to the conclusion that CT-interaction (E_{CT}) in the ground state is the dominant stabilizing factor. There is no doubt about the importance of E_{CT} in systems such as pyridine – ICl [12] etc. For weak π-π sacrificial complexes of the present kind, however, theoretical considerations did clearly point towards the dominance of classical *van der Waals* forces [10]. The sometimes observed appreciable ground state dipole moments can in fact also be explained on this basis [12].

We have recently concluded [1] for the benzene-TCNE systems that the observed increase in complex stability with decreasing I^D of the donor does not necessitate the postulate of dominant CT-interaction in the ground state, since the phenomena may equally arise from strong variations in the *van der Waals*-dispersion contribution (E_{disp}) due to strong variations in polarizability (α^D) within the donor series. The arguments given were, however, by no means a proof for the dominance of E_{disp}.

From perturbation theory $|E_{CT}|$ decreases monotonically with I^D. On the basis of *London's* equation $|E_{disp}|$ increases monotonically with I^D, but also with α^D. Hence, if the total stabilization energy decreases with I^D the two energy contributions are not clearly separable since E_{disp} could be decisive and determined largely by the variation in α^D. If, however, for a given series of D the opposite trend were found, the dominance of E_{disp} would be established.

In Fig. 5 a plot of log $^xK_{ap}$ *vs.* I_1^D is shown, indicating an *increase* in stability with *increasing* I_1^D. We conclude that here E_{disp} provides the dominant contribution to the ground state stability of the complexes. We shall not discuss the question as to whether I^D or α^D is mainly responsible for the observed trend since the effects are –
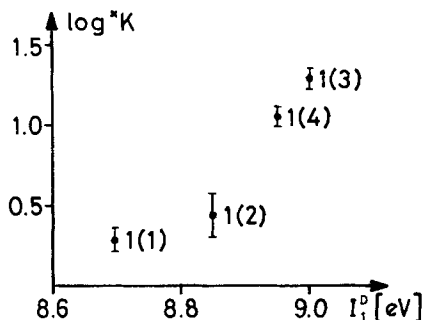

Fig. 5. *Correlation of complex stability* ($^xK_{ap}$) *and donor capacity* (I_1^D)

energetically speaking – very small and furthermore α^D-values for donors of the present kind virtually unknown. Use of additivity schemes for α^D does not seem recommendable given that the amount of 'homoconjugation' changes appreciably within the series as a result of significant changes in distance between the unsaturated units. Though this feature does not manifest itself in the ground state, it bears on the excited states which *inter alia* determine α^D.

The unique fact remains that the present complexes exhibit increasing stability with decreasing donor capacity of the hydrocarbon component (*i.e.* increasing I_1^D), ruling out dominant CT-interaction in the ground state.

3. *Origin of multiple CT-transitions.* Multiple CT-bands were attributed to
- the presence of isomeric complexes [13],
- the transitions from a D-MO to two successive A-MO's [14],
- the transitions from two successive D-MO's to one A-MO [15].

The good correlation of Fig. 4 discussed earlier and involving both CT-transition energies and the first two I^D's of the donors points clearly towards the last explanation for the present diene substrates. This is further illustrated in Fig. 6, where a plot of $\Delta h\nu^{CT}$ (including error limit) (*cf.* Tab. 2) against ΔI^D yields a linear correlation with a coefficient of 0.9488. *Aloisi et al.* [16] were first in trying to settle the question of multiple CT-bands on the basis of PE-data for the donor molecules. The present results together with those for the benzene-TCNE complexes reported in [1] provide further information about this question. They also show that TCNE is an acceptor with an appreciable gap between the LUMO and the next higher unoccupied MO.
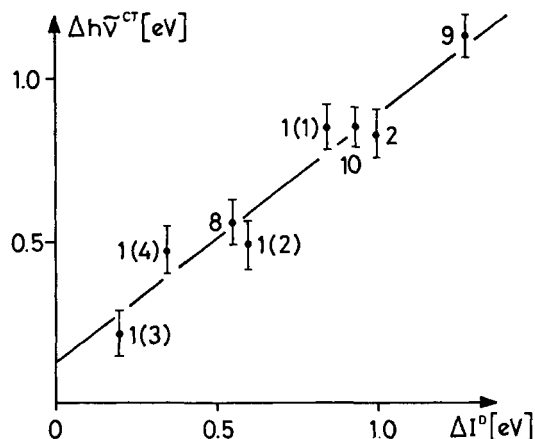
Fig. 6. *Correlation between $\Delta h\nu^{CT}$ and ΔI^D for the dienic donors*

4. *Relative intensity of the two CT-bands and implications for the structure of the complexes.* Using *Mulliken's* approach [8] the ground state $|\psi_0\rangle$ and the two excited states $|\psi_1\rangle$ and $|\psi_2\rangle$ of our systems are given by

$$|\psi_i\rangle = c_{0i}|\psi_0\rangle + c_{1i}|\psi_1\rangle + c_{2i}|\psi_2\rangle; \quad i = 0,1,2$$

$|\psi_0\rangle = A_0\|\psi_D\| \cdot \|\psi_A\|$; no-bond configuration

$|\psi_1\rangle = A_1\|\psi_{D^+}\| \cdot \|\psi_{A^-}\|$; first excited dative configuration   (9)

$|\psi_2\rangle = A_2\|\psi_{D^{+*}}\| \cdot \|\psi_{A^-}\|$; second excited dative configuration

the A-factors being appropriate antisymmetrizers which interchange the electrons between the D- and A-*Slater*-determinants. On this basis the transition moments from the ground to either of the excited states are given by

$$\vec{\mu}_{0i} = \sum_{j=0}^{2}\sum_{k=0}^{2} c_{ji}\, c_{k0}\, \vec{\mu}_{jk} \qquad i = 1,2 \tag{10}$$

where $\vec{\mu}_{jk} = \langle\psi_j|\vec{er}|\psi_k\rangle$.

Consider the following cases:

a) All configurations of (9) belong to the same representation of the point group of the complex. For this case all coefficients in (10) are finite. Furthermore all dipole moments $\vec{\mu}_{ii}$ and transition moments $\vec{\mu}_{ij}$ are also finite since the intermolecular overlap does not vanish by symmetry. Hence both $\vec{\mu}_{01}$ and $\vec{\mu}_{02}$ are also finite; *i.e.* both CT-transitions allowed.

It should however be noted that the term involving $\vec{\mu}_{12}$ may be either finite or vanish.

$$\vec{\mu}_{12} = \langle\psi_1|\vec{er}|\psi_2\rangle = A\langle\|\psi_{D^+}\| \cdot \|\psi_{A^-}\|\vec{er}\|\psi_{D^{+*}}\| \cdot \|\psi_{A^-}\|\rangle \tag{11}$$

It signifies an intramolecular excitation localized within D$^+$, the orbitals involved belonging to the same representation and therefore their direct product being totally symmetric. Depending on the point group of D this local transition is allowed or disallowed.

b) Only one of the excited configurations of (9) belongs to the same representation as the (totally symmetric) no-bond configuration $|\psi_0\rangle$. For simplicity and without loss of generality this former shall be $|\psi_1\rangle$. For this case

$$c_{00}, c_{10}, c_{01}, c_{11} = \text{finite}$$
$$c_{02}, c_{12}, c_{21}, c_{20} = 0 \qquad\qquad (12)$$
$$c_{22} = 1$$

It follows that $\vec{\mu}_{01}$ is still finite. For $\vec{\mu}_{02}$ we obtain from (10) and (12)

$$\vec{\mu}_{02} = c_{10} \cdot \vec{\mu}_{12}$$

the orbitals involved in the local D^+-transition being now definitely of different symmetry. Hence $\vec{\mu}_{02}$ is finite if $D^+ \to D^{+*}$ is allowed, the associated transition $|\psi_0\rangle \to |\psi_2\rangle$ then borrowing intensity from the local one $|\psi_1\rangle \to |\psi_2\rangle$. It is interesting that in this case the transition moment $\vec{\mu}_{02}$ between the preponderant configurations $|\psi_0\rangle$ and $|\psi_2\rangle$ is also finite by symmetry. However, since the intermolecular overlap is zero by symmetry, $\vec{\mu}_{02}$ is not able to contribute to $\vec{\mu}_{02}$. Note that the application of group theoretical considerations for intermolecular CT-transitions is not as straight-forward as for intramolecular ones, as long as one does not depart from *Mulliken*'s resonance formalism in favour of a 'supermolecule' approach.

c) None of the excited configurations of (9) belongs to the same symmetry representations as $|\psi_0\rangle$. For this case $c_{0i} = 0$ for all i in (10). It is trivial to show that here $\vec{\mu}_{01} = \vec{\mu}_{02} = 0$.

In Fig. 7 three conceivable high-symmetry structures for the diene-TCNE complexes are shown. In the C_s-structure TCNE may be either in an *exo*- or *endo*-position

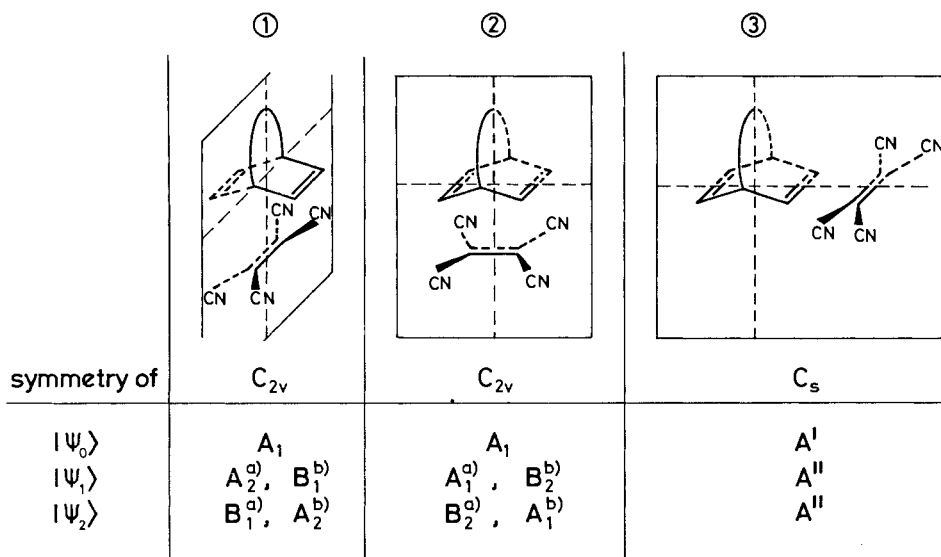| symmetry of	① C_{2v}	② C_{2v}	③ C_s
$|\Psi_0\rangle$	A_1	A_1	A'
$|\Psi_1\rangle$	$A_2^{a)}, B_1^{b)}$	$A_1^{a)}, B_2^{b)}$	A''
$|\Psi_2\rangle$	$B_1^{a)}, A_2^{b)}$	$B_2^{a)}, A_1^{b)}$	A''

Fig. 7. *Conceivable high symmetry structures for the diene-TCNE complexes; symmetry species of the no-bond and the lowest two dative configurations*
a) for **1** (n) (n = 1, 2). b) for **1** (n) (n = 3, 4); for **2**

with respect to the hydrocarbon double bond. Inspection of the corresponding configurational symmetries shows that – according to the discussion above – only the endo-structure ② leads to two allowed transitions.

Further arguments for an *endo*-position of A are:

– The stability of the complex **7**A is higher than that of **1**A. This indicates that the bulky apical substituents in **7** do not interfere with A. That such an interaction may indeed be destabilizing is demonstrated by the fact that **6**A is less stable than **3**A. Apparently, here, A prefers an *exo*-position. *Brown et al.* have come to the same structural conclusion for the Ag⁺-complex of **6** and **3** in view of the longer retention time of **3** in a AgNO₃-coated GLC. column [17].

– An X-ray structural analysis of the **1**(1)-PtCl₂ complex shows the metal in an *endo*-position, the complex exhibiting C_{2v}-symmetry [18].

There is, however, a problem with the structural proposal according to ②. As mentioned before a dominant contribution to the total binding energy of the present weak complexes is certainly provided by dispersion forces. If so, the components will prefer an alignment with the largest principal axes of polarizability parallel to each other[4]). This undoubtedly is true for structure ①, which conflicts with the above conclusion based on symmetry arguments. It thus seems that either the theoretical model used for the prediction of the transition moments is too simplified, or the observed spectra stem from complexes with lower symmetry than visualized. The latter possibility may be extended to the proposal that a whole variety of isomeric, structurally different complexes contribute to the CT-intensity. This conclusion is in line with the earlier discussed finding of significant contact contribution to the measured absorbances of the present systems, including in particular the monoene-complexes. Indeed here, for stability reasons, a parallel arrangement of the double bonds is favoured, which however would result in a zero transition moment. We conclude that structural conclusions based on symmetry arguments and transition probabilities are therefore bound to fail. From the stability of the sterically hindered complexes mentioned above, however, we propose an *endo*-structure for the dienic and an *exo*-structure for the monoenic complexes.

5. *Reaction of the bicyclic dienes with TCNE*. **1**(1) and **1**(2) react with TCNE in CH_2Cl_2 in a [2s + 2s + 2s] *homo-Diels-Alder* fashion.
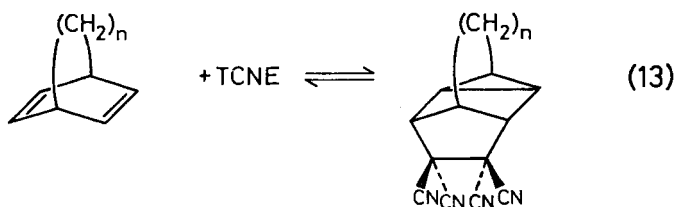
For **1**(1) this reaction was already observed earlier [20]. For **1**(3) and **1**(4) no adduct was found under a variety of conditions.

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[4]) For **1** (1), the axis of largest polarizability is the x-axis [19].

The rates of the observed addition reactions were monitored by the disappearance of the CT-bands of the intermediate complexes[5]). The reactions were pseudo-first order in the complex concentrations, D being always present in large excess.

$$-\frac{d\,[DA]}{dt} = k_{exp}\,[DA] = k'_{exp}\,[D]\,[DA] \tag{14}$$

The results are given in Tab. 3. Several points are worthy of discussion:

i) The reactivity of the bicyclic dienes 1(n) qualitatively decreases with increasing n as indicated by the decrease of k'_{exp} (at 25°, comparable [D]). This parallels the

Table 3. *Rate constants for the disappearance of the EDA-complexes of* **1** (1), *and* **2** *with TCNE in* CH_2Cl_2 (For explanation of symbols see text)

	[D] (mol · l⁻¹)	$10^4\,k_{exp}$ (s⁻¹)	$10^4\,k'_{exp}$ (l mol⁻¹ s⁻¹)
1 (1) at 25° C	0.98	3.85	3.92
	1.97	7.58	3.85
	3.95	12.13	3.07
1 (1) at 0° C	2.03	3.03	1.49
1 (2) at 25° C	1.46	1.16	0.8
	2.42	1.10	0.46
1 (3) at 25° C		no reaction observed	
1 (4) at 25° C		no reaction observed	
2 at 25° C	0.42	3.61	8.53
	0.85	6.37	7.53
	1.06	7.14	6.75
	1.59	9.73	6.14
2 at 0° C	0.43	1.92	4.42
	0.87	4.15	4.77
	1.09	5.45	5.01

increase in I_1^D along the series (up to n = 3) (Fig. 1). From simple perturbation theory this behaviour is expected since reactivity decreases with increasing gap between the HOMO of the donor and the LUMO of the acceptor. Once more it follows that charge transfer is important in determining the heights of the barrier towards chemical bond formation. Clearly, in the transition state there is strong intermolecular overlap between the addends. We recall that the stability of the DA-complexes showed an opposite trend with respect to I_1^D, indicating that charge transfer is not important for the stabilization of the loose EDA-aggregates. Here, intermolecular overlap is of course minute.

ii) Thermochemical estimates (including in particular a consideration of strain effects) [21] suggest that the exothermicity of the above addition reactions decreases with increasing n. The observed reactivity pattern thus also follows from the *Bell-Evans-Polanyi* principle [22]. In addition the estimates for ΔH^0, ΔS^0 indicate in fact
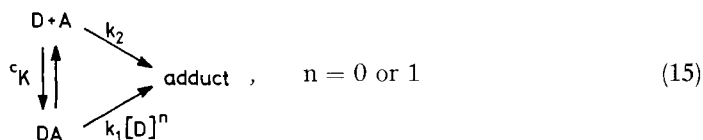
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[5]) The rates obtained by measurement at several different wavelengths were equal.

that the equilibrium (13) for **1**(3) and even more probably for **1**(4) lies on the side of the addends. This would explain the observation, that for these two systems no addition was observed. In this respect it is interesting to note that **1**(2) does not react with TCNE at 200°[6]). Presumably, at this temperature, the positive $-T\Delta S^0-$ overrides the negative ΔH^0-contribution to the free energy and the equilibrium (13) is shifted towards the addends.

iii) For the mechanism of adduct formation the following elementary steps have been visualized [23]:

– collapse of the DA-complex;
– bimolecular reaction of free D and A;
– bimolecular reaction of DA with free D.

The rate expression for either of these processes or any combination of them have been derived by *Rappoport* [23]. His results can be summarized by

$$
\begin{array}{c}
\text{D+A} \xrightarrow{\ k_2\ } \\
{}^cK \updownarrow \qquad\qquad\quad \text{adduct}\ , \qquad n = 0\ \text{or}\ 1 \qquad\qquad (15)\\
\text{DA} \xrightarrow{\ k_1[\text{D}]^n\ }
\end{array}
$$

which leads to the general expression for k'_{exp} as defined in (14)

$$
k'_{exp} = \frac{k_1\ {}^cK\ [\text{D}]^n + k_2}{1 + {}^cK\ [\text{D}]}\ , \qquad n = 0\ \text{or}\ 1 \qquad\qquad (16)
$$

From eq. (16) the six kinetic schemes discussed in [23] follow with

scheme a) : $k_2 = n = 0$
      b) : $k_1 = 0$
      c) : $k_2 = k_1,\ n = 1$
      d) : $k_2 = 0,\ n = 1$ (17)
      e) : $n = 0$[7])
      f) : $n = 1$

From Tab. 3 it follows that k'_{exp} decreases with increasing [D] which immediately excludes schemes c) and d). A plot of $(k'_{exp})^{-1}$ *vs.* [D] is strongly nonlinear for **1**(1) (25°). For **1**(2) (25°) only two measurements are available; if a linear function between $(k'_{exp})^{-1}$ and [D] is assumed, the value ${}^cK = -6.2\ 1\ mol^{-1}$ obtained from slope and intercept bears no relation to ${}^cK = 0.188\ 1\ mol^{-1}$ from the *B–H* treatment (*cf.* Tab. 1). These observations exclude in addition the models a), b) and e). Hence, within the mechanistic framework of eq. (15), scheme f) is left for the present substrates, where formation of the adduct occurs by both routes: bimolecular reaction of D and A as well as bimolecular reaction of the complex with a free D-molecule.

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[6]   Private Communication of Prof. *C. Grob*, Basel.
[7]   Note that in [23] the expression for scheme e) is faulty.

This conclusion has to be considered as tentative, the collected data being admittedly rather limited. We are currently performing further work directed in particular to settle the question if the observed trend in k'_{exp} may perhaps be traced back to strong variations in the dielectric constant of the medium on changing [D].

6. *Reaction of* 2 *with TCNE*. It has been reported that 2 is efficiently dehydrogenated by TCNE furnishing benzene and tetracyanoethane (TCNA) [24]. Dehydrogenation can also be effected by treatment of 2 with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [25]. For the latter reaction it has been recognized that a concerted 1,4-elimination where the two *cis*-hydrogen atoms are transferred directly to the oxygen atoms of DDQ may not take place for reasons of conservation of orbital symmetry [25]. The experimental results were interpreted in favour of a mechanism where simultaneous hydride abstraction by DDQ and proton abstraction by the solvent takes place.

It is obvious that also with TCNE concerted *cis*-dehydrogenation of 2 is a disallowed process[8]). The figure below indicates that this process is also not favorable on a frontier orbital basis. The HOMO of 2 has – as a result of 'through bond' interaction – a_1-symmetry [2].
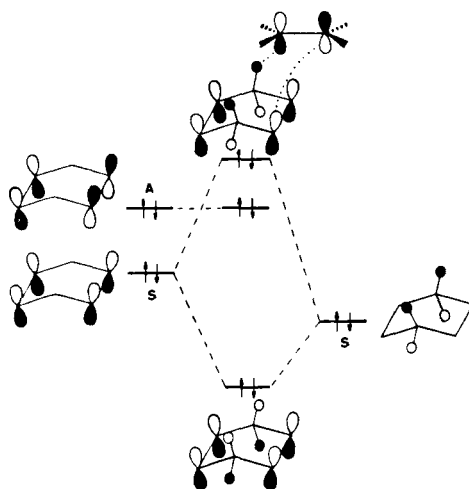
Evidently, its interaction with the LUMO of TCNE vanishes for all complex geometries possessing C_2- or C_s-symmetry. On the other hand interaction between the two orbitals as indicated in the figure leads to a finite matrix element and therefore to a stabilizing contribution. We note that this interaction should initiate 'ene-type' addition of TCNE to 2, leading to 11[9]).

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[8]) On the other hand monomolecular H_2-extrusion from 2 is allowed and is indeed found to occur in a concerted fashion [26].

[9]) An intermediate corresponding to 11 has been earlier postulated to occur in the reaction of 2 with the dimethylester of acetylenedicarboxylic acid, yielding finally (*via* internal *Diels-Alder* addition) a tricyclic addition product ([27].

11
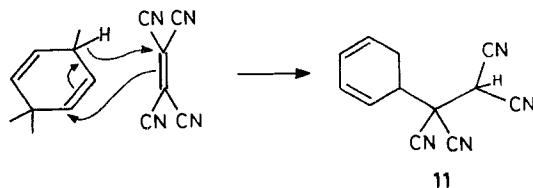
We succeeded in preparing **11** (*cf.* experimental part), a colourless compound which decomposes above 100° to material not further investigated. Above 50°C slow decomposition of solid **11** to benzene and TCNA takes place if it is stored over P_2O_5 under vacuum. The kinetics of formation as well as decay of **11** in CH_2Cl_2-solution is rather complex due to the fact that the **2** · TCNE complex also intervenes as discussed previously for the bicyclic dienes. From the disappearance of the above complex (*cf.* (14)) the rate constants k'_{exp} were obtained at 25° and 0° as a function of [D] (Tab. 3). It is interesting to note that k'_{exp} decreases at high, but increases at low T with increasing [D]. Such a behavior can only be rationalized if a mechanistic scheme according to f) of eq. (17) applies, where two rate constants appear, one being weighted by [D]. The different response of the two constants on changing T then may lead to the observed T-dependence of the reaction.

The matter is complicated by the fact that there is no (1:1)-correspondence between disappearance of starting material and evolution of **11**. We found that the ratio [TCNA]/[**11**] remains roughly constant (= 0.6–0.7) during most of the reaction and is furthermore not significantly dependent on [D]. It appears that consumption of **2** and TCNE is brought about by two parallel reactions: 'ene'-addition and direct dehydrogenation, the pseudo first order lives being 10–30 min for the studied

$$(18)$$
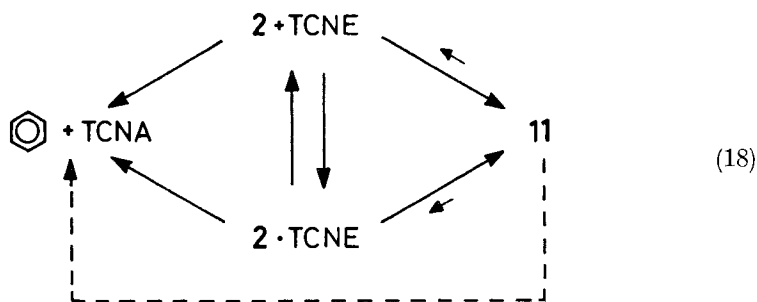
range of [D]. The decay of pure **11** to benzene and TCNA in CH_2Cl_2 or CH_3CN is itself much slower and practically solvent independent. It deviates slightly from first order behaviour at the initial stages of the reaction. Nevertheless, to obtain a rough estimate of the decay kinetics of **11**, we applied a first order treatment which yields a half live of $\sim$ 20 h, *i.e.* the decay of **11** is some 40–120 times slower than its build-up. Solutions of **11** kept 3 days at room temperature contain essentially only benzene and TCNA. If the decomposition is carried out in the presence of quadricyclane (**12**) which is known to scavenge efficiently TCNE [28] one observes after 3 days the product pairs (benzene/TCNA) and (**2**/adduct of **12**-TCNE) in a

roughly (7:1)-ratio. It appears that only a minor fraction of **11** decomposes in a 'retro-ene' fashion, the major portion reacting without liberation of TCNE. The decay of **11** may be strongly enhanced if NH₃-vapour is added, whereas HCl-vapour does not affect the rate. This suggests that the principal path converting **11** to benzene and TCNA consists in a base catalyzed reaction whereby the acidic methin proton of **11** is removed in a first step. The resulting anion undergoes an intramolecular 1,2-elimination, decomposing into benzene and 1,1,2,2-tetracyanoethyl-anion which is reprotonated.

A final comment concerns the surprising observation that **11** does not add TCNE within the timescale of our experiments, though 1,3-cyclohexadiene is known to react rapidly with this dienophile [24] with $\Delta H° = -31$ kcal mol⁻¹ [29]. The additional substituent present in **11** is likely to diminish the exothermicity of the addition reaction, since – as suggested by molecular models – there is some steric crowding in the bicyclic *Diels-Alder* product of **11** with TCNE even in the case of a sterically more favourable *anti*-attack of the latter. Though this effect will presumably not suffice to make the reaction endergonic ($\Delta S° \sim -40$ e.u. [30]) it will decrease its rate. Parallel to this works the deactivating effect of the substituent on the donor capacity of the diene.

We are currently engaged in collecting further data for this system which hopefully leads to a complete elucidation of the reaction mechanism. For the present purpose more important is the finding that **2** and TCNE interact chemically to a major extent in a fashion compatible with simple frontier orbital arguments.

Experimental Part. – *Addition of TCNE to the diene* **1** (2). *Formation of 9,9,10,10-Tetra-cyanoquadricyclo[2,2,2,0²,⁶,2³,⁵]decane.* 3,24 g of **1** (2) and 0,39 g of TCNE were dissolved in 30 ml of CH₂Cl₂. The solution was heated during 10 days under reflux. After removal of the volatile components the residue was twice recrystallized from ethanol. The adduct (1 g = 14% yield) had m.p. 237–238° and decomposed above 240°. – NMR. (DMSO-d₆/CDCl₃, δ-values in ppm rel. TMS): 3.52 (s, 2H); 2.14 (s, 1H); 1.78 (m, 4H); 1.64 (d, 2H); 1.29 (t, 1H). – MS. (m/e-values): 234 (M⁺), 106 (M⁺ – TCNE).

Calc. C 71.78 H 4.30 N 23.92% Found C 71.73 H 4.10 N 23.69%

Addition of TCNE to the diene **2**. *Formation of 5-[1′,1′,2′,2′-tetracyanoethyl]-1,3-cyclohexadiene* (**11**). 128 mg TCNE and 380 mg **2** were dissolved in 50 ml CH₂Cl₂. The solution was kept at RT. for 24 h until its initial colour had disappeared. After removal of the volatile components by vacuum without heating, the residue was extracted by rigorously dried CCl₄. **11** was twice recrystallized from CCl₄ and obtained in colorless plates. It decomposed above 100°. – NMR. (CD₃CN, δ-values in ppm rel. TMS): 6.4 (m, 1H); 6.0 (m, 3H); 5.30 (s, 1H); 3.40 (m, 1H); 2.70 (m, 2H). – NMR. (benzene-d₆): 5.8 (m, 1H); 5.55 (m, 1H); 5.3 (m, 1H); 5.05 (m, 1H); 2.75 (s, 1H); 2.45 (m, 1H); 1.95 (m, 2H). The shift differences in the two solvents are due to a solvent effect, as evaporation of both solutions gave **11** back. – MS. (m/e-values): 208 (M⁺, weak), 181 (M⁺ – HCN), 180 (M⁺ – H₂CN), 154 (M⁺ – 2HCN), 127 (M⁺ – 3HCN), 100 (M⁺ – 4HCN), 78 (benzene⁺). – UV. (CH₂Cl₂): λmax 265 nm (log ε = 3.6). – IR.: Compatible with structure **11**.

Calc. C 69.22 H 3.87 N 26.91% Found C 69.08 H 3.68 N 26.99%

Kinetical measurements for addition reactions. The rate of disappearance of the starting materials was monitored by the decrease of the CT-bands of the initially formed EDA-complexes. Evolution of the products in the case **2**+TCNE was followed by evaporating all volatile materials at various time intervals at low temperature from the reaction solution, dissolving the solid residue in CD₃CN and determining the relative concentration of **11** and TCNA by NMR. spectroscopy.

The same procedure was applied for the decomposition of **11** in the presence or absence of the TCNE-scavenger quadricyclane. This reaction could also be monitored by the decrease of the $\lambda = 265$ nm band in the optical spectrum of **11**.

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