256. Synthesis and *Diels-Alder* Reactivity of 2,3,5,6-Tetramethylidenenorbornane[1])

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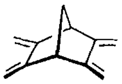
Summary

Pd-catalyzed double carbomethoxylation of the *Diels-Alder* adduct of cyclopentadiene and maleic anhydride yielded the methyl norbornane-2,3-*endo*-5,6-*exo*-tetracarboxylate (**4**) which was transformed in three steps into 2,3,5,6-tetramethylidenenorbornane (**1**). The cycloaddition of tetracyanoethylene (TCNE) to **1** giving the corresponding monoadduct **7** was 364 times faster (toluene, 25°) than the addition of TCNE to **7** yielding the bis-adduct **9**. Similar reactivity trends were observed for the additions of TCNE to the less reactive 2,3,5,6-tetramethylidene-7-oxanorbornane (**2**). The following second order rate constants (toluene, 25°) and activation parameters were obtained for: **1**+TCNE→**7**: $k_1=(255\pm5)\ 10^{-4}$ $\mathrm{mol^{-1}\cdot s^{-1}}$, $\Delta H^{\neq}=(12.2\pm0.5)$ kcal/mol, $\Delta S^{\neq}=(-24.8\pm1.6)$ eu.; **7**+TCNE→**9**, $k_2=(0.7\pm0.02)\ 10^{-4}$ $\mathrm{mol^{-1}\cdot s^{-1}}$, $\Delta H^{\neq}=(14.1\pm1.0)$ kcal/mol, $\Delta S^{\neq}=(-30\pm3.5)$ eu.; **2**+TCNE→**8**: $k_1=(1.5\pm0.03)\ 10^{-4}$ $\mathrm{mol^{-1}\cdot s^{-1}}$, $\Delta H^{\neq}=(14.8\pm0.7)$ kcal/mol, $\Delta S^{\neq}=(-26.4\pm2.3)$ eu.; **8**+TCNE→**10**: $k_2=(0.004\pm0.0002)\ 10^{-4}$ $\mathrm{mol^{-1}\cdot s^{-1}}$, $\Delta H^{\neq}=(17\pm1.5)$ kcal/mol, $\Delta S^{\neq}=(-30\pm4)$ eu. The possible origins of the relatively large rate ratios k_1/k_2 are discussed briefly.

Introduction. - *Florey & Vogel* have presented in 1975 the synthesis of 2,3,5,6-tetramethylidenenorbornane (**1**) in eight steps starting from the *Diels-Alder* adduct **3** of cyclopentadiene and maleic anhydride [1]. The key synthetic intermediate was a norbornane-2,3,5,6 tetracarboxylate successively transformed into the corresponding tetrol, tetratosylate and finally into the tetraene **1**. Five steps were necessary to transform **3** into a mixture of the isomeric methyl norbornane-2,3,5,6 tetracarboxylates. We report now a more efficient synthesis of **1** based on *Stille*'s double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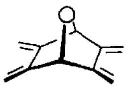
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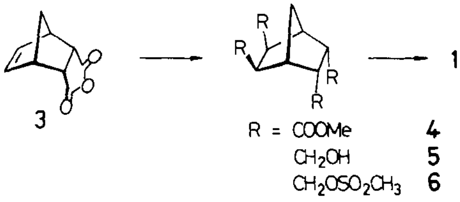
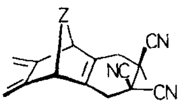
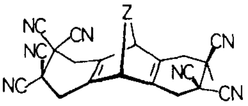
carbomethoxylation [2] of **3** yielding in one step the methyl norbornane-2,3-*endo*-5,6-*exo*-tetracarboxylate (**4**) according to a technology recently developed for the preparation of the oxa-tetraene **2** [3]. The latter is a useful intermediate for the preparation of polycyclic polyfunctional systems, including anthracycline derivatives [4]. This was possible because the addition of the first equivalent of a strong dienophile yielding the corresponding monoadduct occurs at least 100 times faster than the addition of the second equivalent of dienophile, thus allowing the isolation of the monoadduct in good yield without contamination by the 'symmetrical' bis-adduct [5] (see however the addition with dehydrobenzene [4b]). We measured the rate constant of the *Diels-Alder* addition of tetracyanoethylene (TCNE) to the tetraenes **1**,**2**(k_1), and their monoadducts **7**,**8**(k_2), yielding the corresponding bis-adducts **9**,**10**, and evaluated the activation parameters of these reactions. The relatively large reactivity difference k_1/k_2 observed will be discussed and compared with the *Diels-Alder* reactivity of related exocyclic dienes.

Results. – Under 4 atm. of CO and the presence of 6 mol-equiv. of $CuCl_2$ in dry MeOH and a catalytical amount of $PdCl_2$, the norbornene **3** was bis-carbomethoxylated and esterified to the tetraester **4** (87%). The excess of oxidant was necessary to consume the water formed by esterification of **3** [3]. The *syn-exo* bis-carbomethoxylation was expected for a norbornene derivative [2] [3]. The structure of **4** was confirmed by the ^{1}H-NMR. spectrum showing 2 singlets for the methyl esters (3.68 and 3.71 ppm). The H-atoms H–C(5,6-*endo*) gave a doublet at 3.44 ppm with a typical W-long-range coupling constant of 2 Hz with H(*anti*)–C(7) [6]. A doublet of doublet was observed at 3.1 ppm for H(*exo*)–C(2,3) and a multiplet at 2.9 ppm for the bridgehead H-atoms H–C(1,4). Double irradiation as well as H/D exchange experiments in $MeOD/K_2CO_3$ (H–C(2,3,5,6) were exchanged faster than the ester were isomerized) confirmed the ^{1}H-NMR. signal attributions and the structure of **4**.





Z = CH_2 **7**
Z = O **8**



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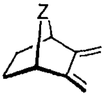
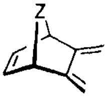
The $LiAlH_4$/THF reduction of **4** yielded the tetrol **5** (74%) that was mesylated into **6** (57%). Quadruple elimination of mesylic acid (*t*-BuOK/DMF/HMPTA) furnished the tetraene **1** (77%, overall yield from **3**: 28%)^{4,5}).

In the presence of one mol-equiv. of TCNE, **1** yielded the monoadduct **7** that could be isolated pure. In the presence of more than 2 mol-equiv., the bis-adduct **9** was formed. No other product could be detected. The second order rate constants of these cycloadditions (k_1, k_2) measured at various temperatures allowed the evaluation of the activation parameters [8], which are reported in the *Table* together with those obtained for the additions of TCNE to the ether analogs **2**, **8**, to 2,3-dimethylidenenorbornane (**11**) and 5,6-dimethylidene-2-norbornene (**12**). Preliminary results with the 7-oxanorbornanes **13** and **14** gave $k \cong 5 \cdot 10^{-4}$ mol$^{-1} \cdot$ s^{-1} and $\leqslant 0.5 \cdot 10^{-4}$ mol$^{-1} \cdot$ s^{-1}, respectively, for their cycloaddition to TCNE in toluene at 298 K.



Z = CH_2: **11**
Z = O : **13**



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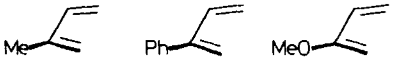
The reactions were followed for at least 3 half-lives and were found to obey pseudo-first order rate laws (k'^{I}) for the disappearance of the TCNE-toluene complex (λ_{max} = 405 nm) when a 15 to 1000-fold excess of the tetraenes **1**, **2** or dienes **7**, **8**, **11**, **12** was used. There was no observable effect on the second order rate constant due to changes of the initial concentration of the cycloaddents ([TCNE] = (1.0–4.7) $\cdot 10^{-4}$ M; ['diene'] = $1.5 \cdot 10^{-3}$ to $1.9 \cdot 10^{-1}$ M) or due to changes in their initial concentration ratios.

Discussion. – The relatively large rate ratio $k_1/k_2 = 364$ measured at 25° for the TCNE addition to **1** *vs.* **7** and $k_1/k_2 = 375$ for TCNE + **2** *vs.* TCNE + **8** are somewhat surprising considering that we are dealing with remote substituent effects on the *Diels-Alder* reactivity of exocyclic dienes grafted onto similar, rigid skeletons. These effects must be compared with the following *Diels-Alder* additions involving changes of the substituent attached directly to the diene function:



(TCNE/CH_2Cl_2/20°)$k^{\mathrm{II}}_{\mathrm{rel}}$: (1.0) ~4.4 ~40 [10]

Part of the rate retardation effect observed when going from the cycloadditions of the tetraenes **1**, **2** to those of the corresponding mono-adducts **7**, **8** is due to a change in the $\Delta S^{\neq}$ term which contribute by about 5 to 20 to the rate ratio k_1/k_2.

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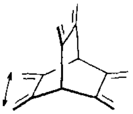
[4]) Chlorination of **5**, as well as the quadruple elimination of HCl on the corresponding tetrachloride were sluggish in contrast to the analogous reactions used in the synthesis of **2** [3].

[5]) For the electronic properties of **1**: [1] [7].

This makes a 'corrected' $k_1/k_2 \simeq 20$ to 80 due to the change in the $\Delta H^{\neq}$ term. A rate retardation effect is also observed when comparing the *Diels-Alder* reactivity of the simpler trienes **12** and **14** with that of the dienes **11** and **13**, respectively (see *Table* and the cycloadditions with methyl acetylenedicarboxylate [11]).

A priori, the *Diels-Alder* reactivity of TCNE in toluene to exocyclic butadienes can be affected by the following factors: *1*) geometry of the diene (1,4-distance ($d_{1,4}$ between the exocyclic methylidene C-atoms [12], conformation of the diene [13]), *2*) polarizability of the diene [14] (ionization potentials, IP. [15], and *3*) exothermicity of the reactions (the *Bell-Evans-Polanyi* principle can be followed [16]!).



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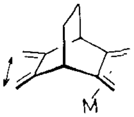

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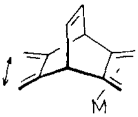

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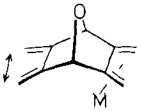


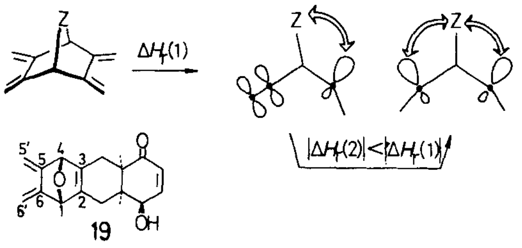
18 M=Fe(CO)$_3$

$d_{1,4}$: 3.066 (2) [17] 3.037 (6) [18] 3.055 (5) [19] 3.159 (8) [20] Å

X-Ray diffraction of the compounds **15**–**18** demonstrates that the 1,4-distance between the methylidene C-atoms of the exocyclic diene does not vary significantly when one of the bridges of the bicyclic skeleton varies from an exocyclic diene to an endocyclic double bond. In the crystal, the [2.2.2]hericene (**15**) [21] has the D_{3h} symmetry, *i.e.* planar dienes. *A fortiori*, this must also be the case for the more rigid norbornane derivatives **1**, **2**, **7**, **8**, **11**–**14**. Therefore, the rate ratio k_1/k_2 cannot be attributed to differential-geometry factors between the tetraenes **1**, **2** and their monoadducts **7**, **8**.

The LUMO localized on the endocyclic double bonds of **7**, **8**, **12** and **14** are expected to stabilize the HOMO of the homoconjugated dienes. This seems to be verified when comparing the IP of the trienes **12** [9], **14** [22] with those of the dienes **11** [7] [9], **13** [7] [22] and tetraenes **1**, **2** [7]. However, the measured IP differences (see *Table*) are very small and might not be significant if there were an experimental error of ±0.05 eV in the IP (see also [23]). The lower reactivity of the 7-oxanorbornane derivatives compared with that of the hydrocarbon analogs is due to the inductive effect of the ether bridge, as indicated by the IP.

The exothermicities of the cycloadditions discussed here have not been measured. Nevertheless, we estimate the additions of TCNE to **12**, **14** to be less exothermic than the reactions TCNE + **11**, **13** because of the 'extra' strain of norbornadiene (oxanorbornadiene) compared with norbornene (oxanorbornene) [24]. The strain increase due to unsaturation of the norbornane skeleton has been ascribed to bond angle deformation about the sp^2 C-atom [25]. If this interpretation were correct, we would expect no significant difference between the exothermicities of the reactions **1**, **2** + TCNE → **7**, **8** (ΔH_r (1)) and **7**, **8** + TCNE → **9**, **10** (ΔH_r (2)). However, we have shown recently that the endocyclic double bond in the 5,6-dimethylidene-7-oxa-2-norbornene derivative **19** [5] has its electron density polarized towards the *exo*-face, making the endocyclic double bond deviate significantly



from planarity, whereas the exocyclic diene plane C(5,5',6,6') does not deviate from the C(1,6,5,4) plane. This makes the O-bridge of **19** tilt away from the endocyclic double bond because of the O(7)↔π(2,3) electronic repulsion. Similar effects have been found for the $H_2C(7)$-bridge of 2-norbornene derivatives [26] [27]. Thus, when transforming the trienes **7**,**8** (as well as **12**,**14**) into norbornadiene derivatives, we expect the new endocyclic double bond to push the $H_2C(7)$ and O(7) bridges back to a 'more symmetrical' position. This gives a picture of the 'extra' strain expected for the dienes **9** and **10** when compared with the trienes **7** and **8**, respectively. It makes the reactions **7**,**8**+TCNE→**9**,**10** less exothermic, and consequently slower, than the additions **1**,**2**+TCNE→**7**,**8**.

Conclusion. - The relatively large rate ratio k_1/k_2 measured for the two successive *Diels-Alder* additions of a strong dienophile to the exocyclic tetraenes **1** and **2**

Table. *Kinetic data of cycloadditions of tetraenes* **1**,**2**, *their monoadducts* **7**,**8**, *2,3-dimethylidenenorbornane* (**11**) *and 5,6-dimethylidene-2-norbornene* (**12**) *to TCNE in toluene*

Diene	k^{II} [10^4 mol^{-1} · s^{-1}] Statistical standard deviation[a]) Temperature of the measurements above (K)					$\Delta H^{\neq}$ kcal/mol (T_m)	$\Delta S^{\neq}$ cal/mol · K (ΔT)	k^{II}(298K) inter- or extra-polated [10^4 mol^{-1} · s^{-1}]	IP [eV]
1 (k_1)	93.3	180	359	683	1180	12.2	−24.8	255	8.34 [7]
	±1.5	±2	±5	±8	±15	±0.5	±1.6	±5	
	285.1	293.4	302.6	312.1	321.2	303	36.1		
7 (k_2)	0.98	2.3	4.1	8.2	15	14.1	−30.1	0.7	
	±0.01	±0.03	±0.05	±0.1	±0.2	±1.0	±3.4	±0.02	
	302.6	312.1	321.2	330.5	340.0	321	37.4		
2 (k_1)	0.945	2.25	4.9	10.4	20.5	14.8	−26.4	1.5	8.60 [7]
	±0.005	±0.05	±0.1	±0.2	±0.2	±0.7	±2.3	±0.04	
	293.4	302.6	312	322.4	331.7	312	38.3		
8 (k_2)	0.08	0.46	1.6			17	−30	0.004	
	±0.002	±0.03	±0.04			±1.5	±4	±0.0002	
	331.8	354.8	372.8			353	41		
11	125	269	512	979	1870	10.9	−27.3	690	8.42 [7]
	±1	±1	±4	±20	±10	±0.6	±2.2	±10	
	272.7	283.9	293.4	302.5	313	293	40		
12	15.5	34.8	69.4	138	265	12.3	−27.7	53	8.48 [9]
	±0.4	±0.2	±0.2	±1	±2	±0.3	±0.9	±0.2	
	283.2	293.4	302.6	312.9	323	303	40		

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[a]) For 6 to 10 independent measurements with 3-5 differents solutions of the dienes and TCNE.

is due to a change of the $\Delta S^{\ddagger}$ term, on one hand, and to a change of the $\Delta H^{\ddagger}$ term, on the other. The latter effect is attributed to a differential effect in the homoconjugative and hyperconjugative interactions between exocyclic dienes and endocyclic double bonds. A change in the exothermicities of the cycloadditions may significantly affect the $\Delta H^{\ddagger}$ term6).

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Experimental Part

General remarks. Kinetic measurements, see [8].

*Methyl norbornane-2,3-*endo*-5,6-*exo*-tetracarboxylate* (**4**). The cyclopentadienemaleic anhydride adduct (**3**, 56.5 g, 0.34 mol), dry $CuCl_2$ (288 g, 2.14 mol), $PdCl_2$ (5 g, 0.028 mol) and dry methanol (1000 ml) were placed in a 2 l Pyrex flask (*Parr* apparatus). After careful degassing, the mixture was pressurized with CO (4 atm.) and stirred for 2 days at RT.; the CO pressure was maintained at 3-4 atm. After removal of the solvent *i.V.*, water (300 ml) and $CHCl_3$ (300 ml) were added. The solid was filtered off *(Celite)*. The aqueous phase was extracted with $CHCl_3$ (3× 50 ml). The organic phases were reunited and washed with a sat. solution of $NaHCO_3$ (3× 50 ml), then with water (3× 100 ml: disappearance of the blue color). After drying ($MgSO_4$), the solvent was evaporated *i.V.* and the crude tetraester was recrystallized from methanol. Yield: 98 g (87%), colorless crystals, m.p. 182-183°. - UV. (CH_3CN): end absorption, $\varepsilon_{215} = 250$. - IR. (KBr): 3040, 3010, 2960, 2910, 2860, 1750, 1730, 1460, 1440, 1370, 1350, 1310, 1270, 1260, 1240, 1200, 1180, 1150, 1130, 1100, 1050, 1040, 1000, 920, 870, 780. - ^1H-NMR. ($CDCl_3$): 3.71 (*s*, 6 H); 3.68 (*s*, 6 H); 3.44 (*d*, $J=2$, 2 H, H−C(5,6)); 3.1 (*d*×*d*, 2 H, H−C(2,3)); 2.9 (*m*, 2 H, H−C(1,4)); 2.3 (*d*×*m*, $J=11$, 1 H, H(*syn*)−C(7)); 1.5 (*d*×*m*, $J=11$, 1 H, H(*anti*)−C(7)). - ^{13}C-NMR. ($CDCl_3$): 173.0 (br. *s*, C=O); 171.7 (br. *s*, C=O); 51.3 (*qa*, 147, CH_3OOC); 45.7 (br. *d*, 134, C(2,3)); 44.4 (br. *d*, 141, C(5,6)); 42.9 (*d*×*d*, $^1J(C,H)=150$, $^3J(C(1),H(4))=10$, C(1,4))7); 36.8 (*t*×*t*, 137, $^3J(C,H)=6$, C(7))8). - MS. (70 eV): 297 (1), 269 (3), 268 (2), 266 (3), 265 (13), 264 (79), 238 (8), 237 (42), 236 (63), 232 (12), 210 (4), 209 (17), 208 (24), 205 (29), 204 (25), 183 (38), 151 (90), 114 (29), 113 (100), 91 (19), 59 (64).

$C_{15}H_{20}O_8$ (328.32) Calc. C 54.87 H 6.14% Found C 54.96 H 6.17%

*2,3-*endo*-5,6-*exo*-Tetrakis(hydroxymethyl)norbornane* (**5**). To a vigorously stirred suspension of $LiAlH_4$ (*Fluka*, purum, 10.4 g, 0.275 mol) in dry THF (300 ml) maintained at 0°, a suspension of **4** (31.4 g, 0.096 mol) in dry THF (300 ml) was added dropwise under N_2. The mixture was heated under reflux for 15 h. After cooling to RT., water (20 ml) was added dropwise under vigorous stirring in N_2 (30 min). The mixture was filtered through silica gel (100 g). The solid (SiO_2 + aluminium salts) was extracted with boiling methanol (2× 100 ml). The filtrates were combined and evaporated *i.V.* The residue was recrystallized from methanol. Yield: 15.3 g (74%), colorless crystals, m.p. 164-165°. - UV. (CH_3CN): end absorption, $\varepsilon_{215} = 100$. - IR. (KBr): 3250, 2960, 2890, 2850, 1480, 1460, 1410, 1380, 1350, 1330, 1280, 1260, 1210, 1170, 1120, 1100, 1070, 1020, 940, 840, 720, 700. - ^1H-NMR. (D_2O): 4.0-3.4 (*m*, 8 H); 2.3-1.9 (*m*, 6 H); 1.6 (*d*×*m*, $J=11$, 1 H, H(*syn*)−C(7)); 1.3 (*d*×*m*, $J=11$, 1 H, H(*anti*)−C(7)). - ^{13}C-NMR. (D_2O): 60.6 (*t*, $J=139$); 58.4 (*t*, $J=139$), 41.6 (br. *d*, $J=139$); 41.1 (br. *d*, $J=139$); 38.4 (br. *d*, $J=138$); 33.1 (*t*, $J=134$). - MS. (70 eV): 199 (2), 185 (2), 180 (3), 168 (3), 167 (3), 162 (3), 149 (46), 131 (20), 119 (23), 105 (29), 94 (55), 93 (41), 92 (22), 91 (70), 79 (77), 31 (100).

$C_{11}H_{20}O_4$ (216.28) Calc. C 61.08 H 9.32% Found C 61.21 H 9.35%

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6) Preliminary results for the TCNE additions to 7-isopropylidene-2,3,5,6-tetramethylidenenorbornane ('7,7-dimethyl[2.2.2]hericene') gave a rate ratio $k_1/k_2 \approx 300$ [28] in agreement with the hypothesis that the *Diels-Alder* reactivities of our exocyclic dienes are affected significantly by the exothermicity of the cycloaddition. See also the preliminary results on the reactivity of [2.2.2]hericene (**15**) [21], 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane and 5,6,7,8-tetramethylidenebicyclo[2.2.2]-2-octene [29].

7) The signal attribution was confirmed by proton off resonance irradiations [30].

8) Comparison with the $H_2C(7)$ signal in the ^{13}C-NMR. spectrum of **1** suggest $^2J(C,H) \simeq 0$ Hz.

*2,3-*endo*-5,6-*exo*-Tetrakis(mesyloxymethyl)norbornane* (**6**). Freshly distilled methanesulfonyl chloride (11.4 g, 0.1 mol) was added dropwise to a solution of **5** (2.16 g, 0.01 mol) in dry pyridine (30 ml) maintained at 0°. The mixture was stirred at 50° for 60 h and then added dropwise to a vigorously stirred mixture of ice/water (100 g). The crude **6** was filtered off, washed with ice-cold water (50 ml) and recrystallized from CH_3CN. Yield: 3 g (57%), white solid, m.p. 170–171°. – UV. (CH_3CN): end absorption, $\varepsilon_{215}=4200$. – IR. (KBr): 3060, 3040, 2990, 2950, 1480, 1420, 1340, 1170, 980, 860, 830, 800, 760. – ^{1}H-NMR. (CD_3CN): 4.35 (*m*, 8 H); 3.25 (*s*, 12 H); 2.4 (*m*, 4 H); 2.3 (*m*, 2 H); 1.8 (br. *d*, 1 H); 1.3 (br. *d*, 1 H).

$C_{15}H_{28}O_{12}S_4$ (528.61) Calc. C 34.07 H 5.23% Found C 34.22 H 5.44%

2,3,5,6-Tetramethylidenenorbornane (**1**). Solid *t*-BuOK (*Fluka, pract.*, 9 g, 0.08 mol) was added in small portions to a stirred solution of **6** (3 g, 0.0057 mol), dry DMF (90 ml) and HMPTA (15 ml). The mixture was stirred at 80° for 72 h. After cooling to RT., water (50 ml) was added dropwise and the tetraene **1** was extracted with pentane (4×50 ml). The organic extract was washed with water (5×100 ml), dried ($MgSO_4$) and evaporated *i.V.* The crude **1** was dissolved in hexane, filtered through a short column of Florisil. Evaporation *i.V.* yielded 0.63 g (77%), colorless crystals, m.p. 28–30°. – UV. (isooctane): 253 (sh., 7900), 246 (sh., 9400), 236 (12500), 228 (12000), 220 (sh., 8900). – IR. (KBr): 3080, 2990, 2930, 2880, 2860, 1780, 1630, 1450, 1420, 1105, 1010, 940, 885. – ^{1}H-NMR. ($CDCl_3$): 5.20 (*s*, 4 H, 4 H(*Z*)); 4.95 (*s*, 4 H, 4 H(*E*)); 3.40 (*t*, *J*=2.5, 2 H, H–C(1,4)); 1.65 (*t*, *J*=2.5, 2 H, $H_2C(7)$). – ^{13}C-NMR. ($CDCl_3$): 149.0 (*s*, C(2,3,5,6)); 101.4 (*t*, *J*=158, $H_2C{=}C(2,3,5,6)$); 54.5 (*d*, *J*=148, C(1,4)); 40.4 (*t*, *J*=138, C(7)). – MS. (70 eV): 144 (72), 129 (77), 128 (100), 127 (26), 117 (14), 116 (13), 115 (42), 104 (4), 103 (7), 102 (5), 91 (54), 89 (8), 85 (9), 83 (13), 78 (8), 77 (14), 65 (24), 63 (17), 51 (23).

$C_{11}H_{12}$ (144.22) Calc. C 91.61 H 8.39% Found C 91.73 H 8.48%

4,4,5,5-Tetracyano-9,10-dimethylidenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (Monoadduct of **1** with TCNE) (**7**). The tetraene **1** (265 mg, 1.8 mmol) and TCNE (235 mg, 1.8 mmol) in dry benzene (10 ml) were stirred at RT. for 15 h (disappearance of the yellow benzene/TCNE complex). The monoadduct **7** was filtered off and washed with cold benzene (3–5 ml) and recrystallized from CH_2Cl_2/pentane 1:1. Yield: 400 mg (80%), colorless crystals, m.p. 185–187°. – UV. (CH_3CN): 247 (sh., 6150), 236 (sh., 10950), 229 (12650), 222 (sh., 11550). – IR. (KBr): 3100, 3005, 2960, 2260, 1775, 1670, 1640, 1440, 885. – ^{1}H-NMR. (CD_3COCD_3): 5.25 (br. *s*, 2 H); 5.00 (br. *s*, 2 H); 3.68 (*d*, *J*=19, 2 H); 3.23 (*d*, *J*=19, 2 H); 2.0 (*d*×*m*, *J*=9, 1 H); 1.7 (*d*×*m*, *J*=9, 1 H). – MS. (70 eV): 272 (46), 245 (4), 220 (9), 194 (7), 193 (10), 167 (8), 144 (100), 129 (89).

$C_{17}H_{12}N_4$ (272.31) Calc. C 74.98 H 4.44% Found C 75.17 H 4.64%

4,4,5,5,11,11,12,12-Octacyanotetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene (Bis-adduct of **1** with TCNE) (**9**). A solution of **1** (20 mg, 0.14 mmol) and TCNE (45 mg, 0.35 mmol) in dry benzene (5 ml) was stirred at 70° for 15 h. After cooling to RT., the bis-adduct **9** was filtered off, washed successively with benzene (2 ml) and CH_2Cl_2 (2 ml) and recrystallized from acetone/hexane 1:1. Yield: 49 mg (89%), colorless crystals, m.p. >200° (dec.). – UV. (CH_3CN): end absorption, $\varepsilon_{215}=1500$. – IR. (KBr): 3050, 2980, 2950, 2880, 2260, 1480, 1440, 1270, 1230, 1220, 680. – ^{1}H-NMR. (CD_3COCD_3): 3.75 (*m*, 2 H); 3.70 (*m*, 8 H); 2.29 (*m*, 2 H). – MS. (70 eV): 400 (13), 346 (11), 272 (20), 271 (14), 218 (19), 149 (17), 144 (20), 119 (42), 117 (45), 91 (25), 64 (58), 46 (100).

$C_{23}H_{12}N_8$ (400.40) Calc. C 68.99 H 3.02% Found C 69.21 H 3.20%

4,4,5,5-Tetracyano-9,10-dimethylidene-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (Monoadduct of **2** to TCNE) (**8**). A solution of **2** [3] (150 mg, 1.03 mmol) and TCNE (130 mg, 1.03 mmol) in dry benzene (5 ml) was stirred at 60° for 15 h. After cooling to 5°, the monoadduct was filtered off, washed with cold benzene (1–2 ml) and recrystallized from CH_2Cl_2/pentane. Yield: 265 mg (94%), colorless crystals, m.p. >200° (dec.). – UV. (CH_3CN): 241 (sh., 6200); 221 (15200); 214 (16500). – IR. (KBr): 3095, 3050, 3000, 2980, 2960, 2940, 2260, 1825, 1640, 1440, 1290, 1235, 1135, 1060, 980, 910, 850, 765. – ^{1}H-NMR. (CD_3COCD_3): 5.33 (*s*, 2 H); 5.24 (*s*, 2 H); 5.20 (*s*, 2 H); 3.83 (*d*, *J*=18, 2 H); 3.35 (*d*, *J*=18, 2 H). – MS. (70 eV): 274 (4), 247 (3), 246 (9), 245 (15), 219 (9), 218 (5), 192 (5), 191 (5), 146 (9), 140 (8), 118 (15), 117 (21), 94 (19), 91 (7), 52 (92), 28 (100).

$C_{16}H_{10}N_4O$ (274.28) Calc. C 70.06 H 3.67% Found C 69.97 H 3.73%

Bis-adduct of **2** to TCNE (**10**), *cf.* [1].

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