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SYNTHESIS AND ELECTROCYCLISATION OF HENDECAFULVADIENES [1)] "AZULENOID" 14π-ANNULENES

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The possibility of a 24π-electrocyclisation has been investigated in the hendecafulvadienes 3 (4); examples of a novel type of bridged 14π-annulene (6,12,13) have been synthesised and shown to have "azulenoid" character.

In the vinylogous fulvalenes (fulvadienes) A - D the electrocyclisation involving all (12-18) π-electrons (α,ω) and antarafacial bond formation is the preferred intramolecular thermal stabilisation. The heptahendeca- (E) and the hendecafulvadiene F (*syn*/*anti*) were envisaged as candidates with potential 20π-and 24π-transition states [1)]. Synthesis and electrocyclisation of dicyano-derivatives of F are the subject of this paper.

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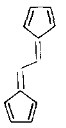

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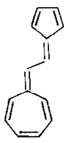

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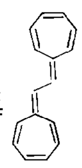

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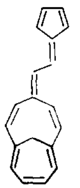

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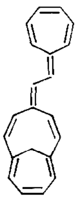

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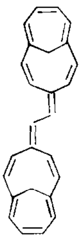
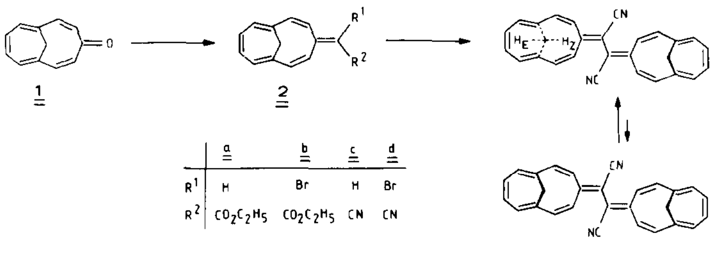


Synthesis of the hydrocarbons F along the lines worked out for C [2,3)] was not pursued in view of the isomer distribution to be expected for nucleophilic additions to the methanocycloundecapentaenylium cation [4)]. Instead the 1,1'-dicyano-compounds 3/4 were prepared by coupling two suitable hendecafulvenes (the procedure used by *Kitahara et al.* in the case of dicyano-C) [5)]. While the ester 2a [1)] could not be brominated to afford 2b, upon reaction with 1.5 equiv. of N-bromosuccinimide (CH_2Cl_2, 0°C, 5 min) the nitrile 2c gave 50-55% of the light red 2d (m.p. 145-148°C, λ_{max}(ethanol)= 394 nm (ε= 10500)). 2c was obtained by *Wittig-Horner*-condensation with 1 ($(C_2H_5O)_2P(O)CH_2CN$, NaH, boiling xylene); the modest yield (32% isolated as orange plates (m.p. 134°C, λ_{max}(ethanol)= 385 nm (ε= 8500)) was due *i.a.* to partial decomposition of the reagent under the necessarily drastic reaction conditions. Treatment of 2d with

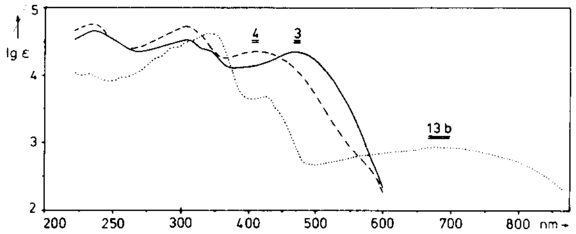


3

4

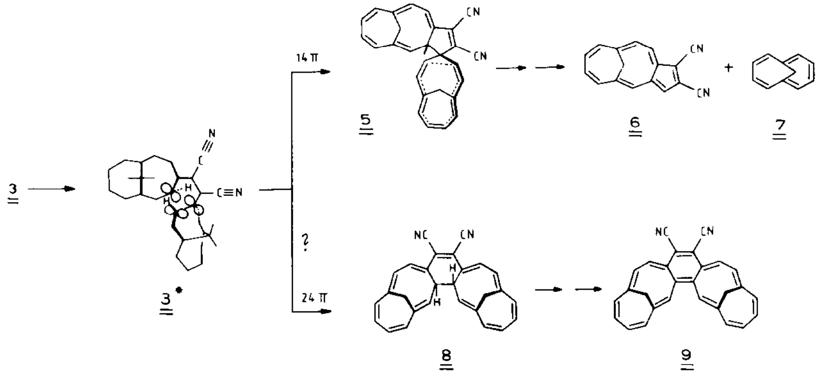
	a	b	c	d
R^1	H	Br	H	Br
R^2	$CO_2C_2H_5$	$CO_2C_2H_5$	CN	CN

activated copper in abs. DMF (90°C, 30 min) affords - under partial reduction (2c) and polymerisation - only one (TLC, ^{1}H-NMR)[7] 1,1'-dicyanohendecafulvadiene (3, 40%, red violet crystals, m.p. 238°C). The use of other metals either meant higher proportions of 2c (Zn, Na) or no reaction (Mg). In solution (possibly under acid catalysis, slowly at 20°C, quickly at 140°C) or in substance (short heating beyond the melting point) 3 equilibrates with 4 (ca. 9:1); such relatively rapid *cis*-/*trans*-isomerisations are known for polar fulvalenes[4]. Upon chromatography pure solutions of 4 can be separated. The ^{1}H NMR spectra of 3/4 are very similar[8]; differentiation of 3/4 rests mainly on the longest wavelength UV/VIS absorption of 468 and 408 nm resp. (Fig.) and a comparison of molecular models based on the known geometry of 1[2].

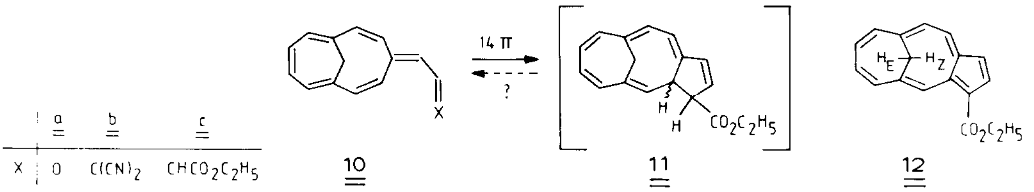


In Scheme 1 a sterically reasonable transition state (3^*) for the α,ω-cyclisation in 3 is depicted: *a priori* it was understood, that the orbital alignments are not as favourable as for A - D and that the 14π-routes are plausible alternatives[9]. And indeed, 3(4) is kinetically much more stable than the lower vinylogues A - D. In 10^{-2}M solutions (tetralin, triglyme) 3(4) remains unchanged up to 190°C. At temperatures between 200° and 500°C only polymerisation occurs. Furthermore in the presence of an oxidising agent (chloranil, MnO_2) no highly coloured annulene (9) or any other monomer is seen (TCL, UV/VIS, ^{1}H NMR). Only upon vapour phase pyrolysis (400°C, 0.01 Torr, contact time ca. 0.1 sec) very small amounts (3-5% each) of two monomeric products are isolated: the green crystalline 6 (1,2-dicyano-5,10-methanocyclopentacycloundecaen (mp. 206°C)) and 7 (methano[10]annulene)[10]. Their formation can be explained with a 14π-cyclisation (3 → 5) followed by fragmentation into the two stable ("aromatic") components[11]. *I.a.* the fast [1,9]-H-migrations[1] e.g. in 5(8), might contribute to the high degree of polymerisation, with consequence that the preferred mode of thermal transformation in 3(4) cannot be elucidated.

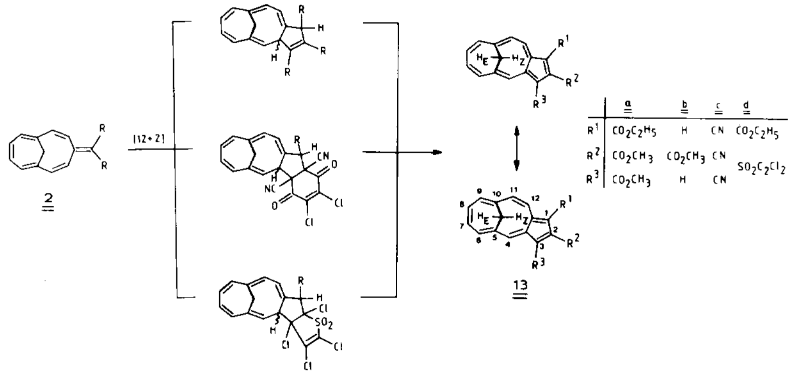
Scheme 1



The usefulness of the electrocyclic route to bridged 14π-annulenes of type 6 has been investigated with the vinylogous methanohendecafulvenes 10b/c, obtained from the aldehyde 10a[1] with malodinitrile (96%, violet needles, m.p. 228-232°C, λ_{max}(ethanol)= 493 nm (ε= 27000)) and $(C_2H_5O)_2P(O)CH_2CO_2C_2H_5$/NaH (60%, orange needles, m.p. 107°C, λ_{max}(ethanol)= 405 nm (ε= 19600)) resp. Thermolysis in solution (150-200°C) or in the vapour phase (200-500°C, 0.01 Torr) leads only to polymeric material. Solution thermolysis of 10c in the presence of MnO_2, however, allows the isolation of 12 as a green oil (5%, λ_{max} (ethanol)= 625 nm (ε= 800)). Clearly, the methanohendecafulvene-unit participates in such electrocyclic reactions only under drastic conditions and gives rise to highly competitive pathways (e.g.[1,9]-H-migrations in 11) [1]. This point is further illustrated by cycloaddition reactions with 2a/c which were pursued as a second pericyclic pathway ([12+2]) to the novel 14π-annulene system. Upon heating in dimethylacetylenedicarboxylate 2a is consumed at 80°C without the appearence of a monomeric adduct. In the presence of MnO_2 25% (not optimised) of the green 13a (m.p. 149-152°C, λ_{max} (ethanol)= 590 nm (ε= 1500)) is obtained [1]. In phosphoric acid (90°C) 13a decarboxylates to 13b (50-55%, green needles, mp. 94°C, λ_{max}(ethanol)= 672 nm (ε= 900)), which is protonated by trifluoroacetic acid to a ca. 1:1-mixture of the conjugate acids resulting from protonation at C-1(3). The tricyano-derivative 13c (10%, green needles, m.p. 270-280° (dec.), λ_{max} (acetonitrile)= 614 nm (ε= 2700)) is formed from 2c with dichlorodicyanoquinone (20°C, CH_2Cl_2)[11], the annellated 13d (5% black green needles, mp. 276°, λ_{max}(acetonitrile)= 670 nm (ε= 1000) from 2a with tetrachlorothiophenedioxide (xylene, 140°C).



	a	b	c
X	O	$C(CN)_2$	$CHCO_2C_2H_5$



	a	b	c	d
R^1	$CO_2C_2H_5$	H	CN	$CO_2C_2H_5$
R^2	CO_2CH_3	CO_2CH_3	CN	$SO_2C_2Cl_2$
R^3	CO_2CH_3	H	CN	

From the NMR-data (^1H-, ^{13}C) [8], with e.g. the chemical shifts of the CH_2-protons ($CDCl_3$, $[D_6]$acetone)*) as a proven criterium [10], the molecules 6,12,13a-d can be characterised as delocalised ("aromatic") 14π-annulenes, in which the substituents influence the polarisation of the basic structure (as approximated by 13b) in a fashion, which is typical for the azulene molecule [13].

	1	2a*	2c	2d	3	4	6	12	13a	13b	13c*	13d
δ_{H_E}	0.03	0.36	0.58	0.33	0.48	0.39	-0.39	-0.50	-0.49	-0.08	-0.23	0.05
δ_{H_Z}	1.59	3.14	3.05	2.71	2.83	2.80	-0.08	-0.06	-0.81	1.13	-0.64	-0.23

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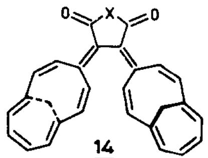
8) The new compounds are characterised by elemental analysis and spectra (MS, IR, UV, ^{1}H-, ^{13}C NMR); e.g: ^{1}H NMR($CDCl_3$; 250 MHz): 3: 5.81(d,10-H)*,6.48(d,1-H)*,6.65-6.84(m,4-,7-H), 6.87(d,9-H)**,7.00(d,2-H)**,7.13-7.26(m,5-,6-H);$J_{4,12Z}=J_{7,12Z}=1.5$,$J_{12E,12Z}=11.2$,$J_{1,2}=J_{9,10}=12.0$Hz;4: 5.97(d,10-H),6.31(d,1-H)*,6.7-6.8(m,4-,7-H),6.92(d,9-H)**,7.01(d,2-H)**,7.13-7.26(m,5-,6-H);$J_{4,12Z}=J_{7,12Z}=1.5$,$J_{12E,12Z}=11.2$,$J_{1,2}=J_{9,10}=12.0$Hz; 12: 7.42(d,11-H),7.48 (d,1-H),7.50(t,7-H),7.54(d,9-H),7.63(t,8-H),7.86(d,6-H),8.24(d, 12-H),8.30(d,2-H),10.08 (s,4-H);$J_{6,13Z}=J_{9,13Z}=1.5$,$J_{1,2}=4.0$,$J_{6,7}=J_{7,8}=J_{8,9}=8.0$,$J_{11,12}=10.5$,$J_{13E,13Z}=11.2$Hz; 13b: $\delta=7.11$(d,11-H),7.23(d,9-H),7.32(dd,7-H),7.52(dd,8-H),7.55(d,6-H),7.74(br.s,3-H)*,7.79(br.s,1-H)*,7.82(d,12-H),8.68(s,4-H);$J_{6,13Z}=J_{9,13Z}=1.5$,$J_{11,12}=10.5$,$J_{6,7}=J_{7,8}=J_{8,9}=8.0$,$J_{13E,13Z}=11.2$. ^{13}C NMR($CDCl_3$): 12: 32.0(C-13),126.2(C-7),127.6(C-11),128.9(C-1),129.2(C-9), 133.2(C-12),133.9(C-8),134.2(C-6),136.0(C-2),146.7(C-4); 13b: 33.3(C-13),125.0(C-1)*, 125.3(C-12),126.7(C-9),128.2(C-6),128.6(C-3)*,132.6(C-7),133.2(C-11),134.5(C-8),148(C-4).

9) We have not yet succeeded in transforming 3(4) into e.g. the anhydride 14 (X=O), in which the stereoelectronic requirements for α,ω-cyclisation appear to be more favourable.



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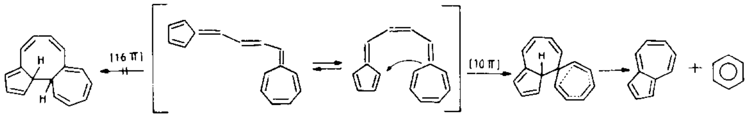
12) Upon vapour phase pyrolysis of the trans-fulvatriene 16 in a presumably similar fragmentation azulene and benzene are formed in 50% yield; no 16π-electrocyclisation (15) is observed (O. Schweikert, Ph.D. Thesis, Univ. Freiburg i. Br. 1980).



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