2,6-Dimethyl Semibullvalene-2,6-dicarboxylates[1]

Helmut Quast*[a], Alexander Witzel[a], Eva-Maria Peters[b], Karl Peters[b], and Hans Georg von Schnering[b]

Institut für Organische Chemie der Universität Würzburg[a],
Am Hubland, W-8700 Würzburg

Max-Planck-Institut für Festkörperforschung[b],
Heisenbergstraße 1, W-7000 Stuttgart 80

The enolized β-oxo ester 9 is reduced by NaB(CN)H$_3$ in weakly acidic methanol solution to afford an almost quantitative yield of a mixture of diastereomeric β-hydroxy esters 10. On treatment with phosphorus oxychloride in pyridine, 10 is converted into a mixture of the β-chloro esters exo-11, endo-11, exo-12, endo-12, and 13 which is separated in part by chromatography. Sodium methoxide in methanol eliminates hydrogen chloride from the crude mixture of β-chloro esters producing the α,β-unsaturated ester 7a in 84% yield based on 9. – Acid-catalysed equilibration of the known vinyl sulphides C$_2$- and C$_S$-15 is carried out on large scale furnishing a 73:27 ratio of C$_2$- and C$_S$-15. This mixture is oxidized to the sulphones C$_2$- and C$_S$-16 which are allowed to react with sodium cyanide supported on aluminium oxide affording the α,β-unsaturated dinitrile 17 which is isolated by chromatography. Thus, 17 is now available on a 30-g scale. Methanolysis of 17 by a prolonged treatment with hydrogen chloride in methanol followed by hydrolysis of the Pinner salt leads to 7b. – Both α,β-unsaturated esters 7a and b are readily brominated at the allylic positions by N-bromosuccinimide to yield the γ,γ'-dibromo esters 19a and b. Zinc-copper couple in tetrahydrofuran converts 19a and b into the semibullvalenedicarboxylates 2a and b. While 2a is persistent only in dilute solutions, thus frustrating all attempts at its isolation, 2b exhibits considerable stability in solution and forms lemon-coloured crystals. The semibullvalenedicarboxylates 2a and b undergo a very rapid degenerate Cope rearrangement in solution. In addition, 2b exhibits reversible thermochromism in both solution and solid state. The structures of the new compounds are based on spectroscopic evidence, including mass, IR, and NMR spectra. The configurations of exo-11, exo-12, 19a and b are established by X-ray diffraction analyses.

The predicted accelerating effect of π-acceptor substituents on the degenerate Cope rearrangement of bridged homotropilidenes, e.g. bullvalenes, barbaralanes, and semibullvalenes[2], was demonstrated for the first time in the barbaralane series, with 2,6-dicyanobarbaralane as the candidate[3,4]. Shortly afterwards, the 2,6-dicyanosemibullvalene 1b has been synthesized[5−7] which not only corroborated this result[6] but also stimulated new interest by exhibiting exceptional properties, such as being yellow in the absence of a chromophor, showing reversible thermochromism[8], and, in the solid state, a rapid non-degenerate Cope rearrangement between valence tautomers non-equivalent only by virtue of their environment in the crystal lattice[9]. The interesting colour and thermochromism of 1b are shared by the 1,5-bridged semibullvalene-2,6-dicarbonitrile 1c[10,11] but not by the 3,7-dicyanosemibullvalene 4a[12−14] nor the corresponding dimethyl 3,7-dicarboxylate 4b[12,15]. Grohmann's series of tetramethyl semibullvalenetetracarboxylates 3 seems to exhibit properties similar to those of the dinitriles 1. Unfortunately, an investigation of the thermochromism of 3 is still lacking, and the determination of the Cope barrier is hampered, apparently, by conformational ambiguities due to the proximity of the ester groups[16]. Surprisingly, the more simple semibullvalene-2,6-dicarboxylates 2 have not been addressed so far. Therefore, we embarked on a study aimed at their synthesis in order to assess the influence of ester groups on the Cope barrier, to find out wether two such groups suffice to induce the extraordinary properties mentioned above, and, finally, to contribute to an understanding of the structural features
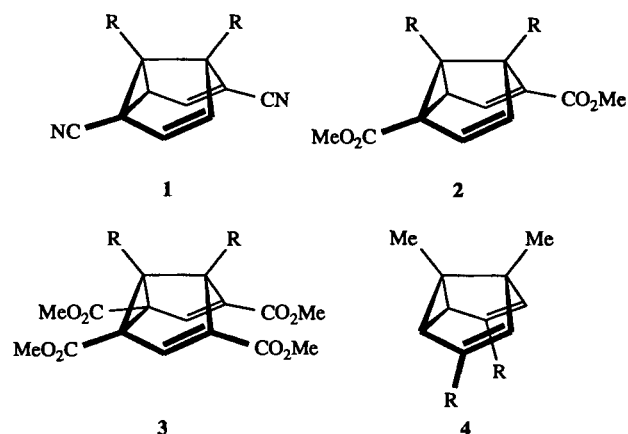
	R		R
1a – 3a, 7a, 19a	H	4a	CN
1b – 3b, 7b, 19b	Me	4b	CO$_2$Me
1c, 3c	(CH$_2$)$_4$		

common to the group of degenerate bridged homotropilidenes possessing unusual properties. Some results are reported here.

The dimethyl bicyclo[3.3.0]octadienedicarboxylate **7a** is required as the starting point for the synthesis of **2a** on the most reasonable route to semibullvalenes pioneered by Askani as early as some twenty years ago[17]. The α,β-unsaturated ester **7a** has been obtained by the isomerization of the β,γ-unsaturated ester **6** which is the product of trapping dilithium semibullvalenediide by carbon dioxide followed by esterification with diazomethane. Because this sequence, which has been disclosed only in a short communication[18], is obviously difficult to adapt to a larger scale, we resorted to a strategy based on the enolized β-oxo ester **8** which is readily available by the Weiss reaction[19,20] of dimethyl 3-oxoglutarate with glyoxal[21].
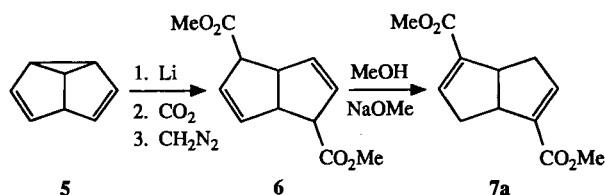

The tetraester **8** has been reported to be decarbalkoxylated by sodium methoxide in dimethyl sulphoxide to afford the diester **9** in 90% yield[22]. In our hands, the yield of this reaction was only modest, unfortunately. Increasing the amount of the reagent, monitoring the course of the reaction by thin-layer chromatography, and improvements of the work-up procedure eventually resulted in a 52% yield on a 0.1-mol scale. Thin-layer chromatography revealed an intermediate which, apparently, is the triester formed in the first decarbalkoxylation step.

Several cyclic β-oxo esters have been reduced to β-hydroxy esters by NaBH₄[23], by NaBH₄ in the presence of bis(triphenylphosphane)palladium(II) chloride[24], or by NaB(CN)H₃ in weakly acidic solution[25]. When the latter procedure was applied to the β-oxo ester **9**, the acidity of the reaction medium was maintained by addition of a solution of hydrochloric acid in dry methanol such as to keep methylorange, employed as an indicator, in its acidic form. The course of the reaction was again monitored by thin-layer chromatography. In this way, an almost quantitative yield of a mixture of diastereomeric β-hydroxy esters **10** was obtained which had neither to be separated nor to be purified for the next step. Dehydration of **10** was attempted by a treatment with phosphorus oxychloride in pyridine[26]. The unexpected result, however, was a complex mixture of β-chloro esters containing only tiny amounts of the α,β-unsaturated ester **7a**. Some of the major components of the mixture were separated by flash chromatography followed by preparative medium-pressure liquid chromatography[27] involving automatic recycling[28]. Thus, *exo*-**11** and *exo*-**12** were obtained in pure form while the attempted separation of **7a** and *endo*-**11**, and of *endo*-**12** and **13** as well, were frustrated by very similar chromatographic properties. Nevertheless, the gross structures of the isolated products, two of

which, viz. *exo*-**11** and **7a**, exhibited C_2 symmetry, could be elucidated by a combination of IR, proton and carbon-13 NMR spectroscopy (Tables 2−7, 9). In particular, the presence of nonconjugated ester groups, as in *exo*-**11**, *endo*-**11**, and **13**, or an α,β-unsaturated ester functionality, as in **7a**, or both ester types, as in *exo*- and *endo*-**12**, was immediately evident from a cursory inspection of the IR and carbon-13 data. The configurations, on the other hand, were difficult to assign on the basis of the available spectroscopic evidence. Therefore, X-ray diffraction analyses of *exo*-**11** and *exo*-**12** have been performed which not only revealed the configuration of the investigated compounds (Figure 1) but also provided the clue for the determination of the other structures by a comparison of NMR data.
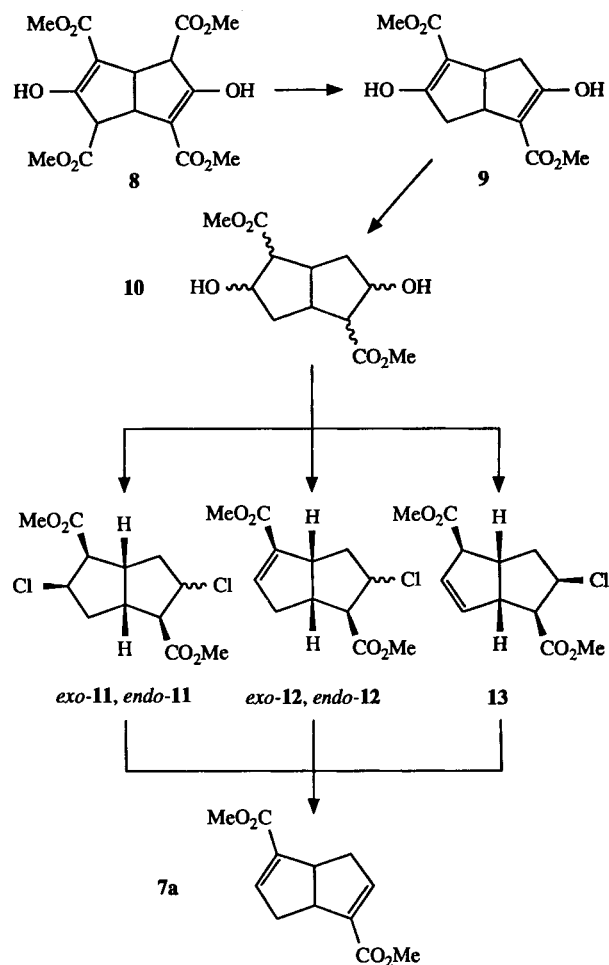
With the results of the phosphorus oxychloride-pyridine treatment of the β-hydroxy ester **10** at hand, it became immediately obvious that a stronger base would convert all compounds formed to the desired α,β-unsaturated ester **7a**. Towards this end, the product mixture of the phosphorus oxychloride-pyridine reaction was treated with a solution of sodium methoxide in methanol. It was gratifying to achieve a 84% yield of **7a** in this way without more elaborate work-up than simple flash chromatography. Thus, the α,β-unsaturated ester **7a** is available from the β-oxo ester **8** in four steps and an overall yield of 43%.

Table 1. Experimental details and results of the X-ray diffraction analyses of the chloro diesters *exo*-11 and *exo*-12 and the dibromo diesters **19a** and **19b**. For atomic parameters see Tables 8, 10—12

Cpd.	*exo*-11	*exo*-12	**19a**	**19b**
Molecular formula	$C_{12}H_{16}Cl_2O_4$	$C_{12}H_{15}ClO_4$	$C_{12}H_{12}Br_2O_4$	$C_{14}H_{16}Br_2O_4$
Molecular mass	295.16	258.70	380.04	408.10
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	Pa	P2$_1$/n	P2$_1$/c	Pbca
a [pm]	1219.7(2)	2048.6(4)	1567.1(2)	1479.7(2)
b [pm]	646.9(1)	698.8(2)	978.0(2)	1824.8(2)
c [pm]	874.5(1)	625.2(1)	929.2(1)	1141.1(1)
β [°]	93.17(1)	92.88(1)	106.86(1)	
V [pm^3] $\cdot 10^{-6}$	688.9(2)	1239.0(5)	1377.5(4)	3081.1(6)
Z	2	4	4	8
d(calcd) [g cm^{-3}]	1.423	1.387	1.832	1.759
Size of crystal [mm]	0.5x0.8x0.2	0.8x1.7x0.3	0.4x0.75x0.2	0.25x0.65x0.2
Range (h)	0 – 15	0 – 26	0 – 20	0 – 19
(k)	0 – 8	0 – 12	0 – 12	0 – 23
(l)	−11 – 11	−8 – 8	−12 – 11	0 – 14
No. of measured reflections	1803	3104	3487	3977
Symmetrie-independent reflections	1651	2849	2977	3537
Observed reflections $F>3\sigma(F)$	1617	2509	2268	2151
Linear absorpt. coeff. [mm^{-1}]	0.87	0.30	5.83	5.22
Absorption correction	ψ-Scan	ψ-Scan	ψ-Scan	ψ-Scan
Ratio $F_{obs.}$/parameters	9.92	16.19	13.83	11.82
R	0.033	0.057	0.059	0.061
R_w	0.033	0.058	0.050	0.042
Diff. Four. $\Delta\rho_{max}$[*] [eÅ^{-3}]	27.08	0.32	0.83	0.62
$\Delta\rho_{min}$[**]	1.62	0.21	0.77	0.69

[*] Maximum and [**] minimum of the remaining electron density in the final differential Fourier synthesis.
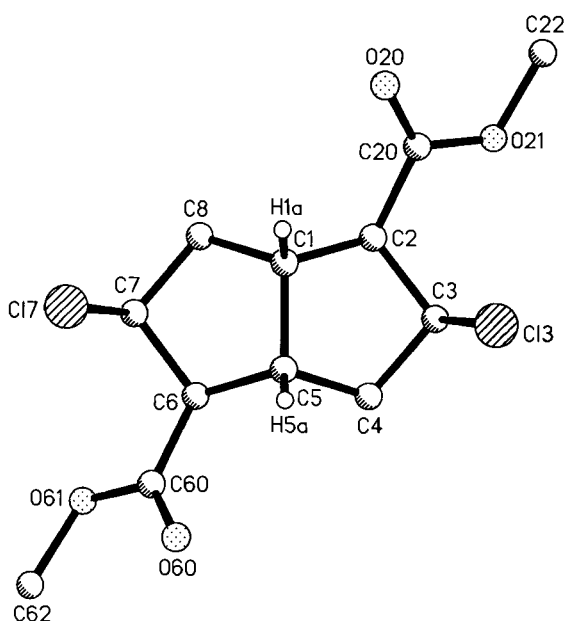

Figure 1. Perspective drawing of the dichloro diester *exo*-11 with the numeration of the atoms corresponding to Table 9
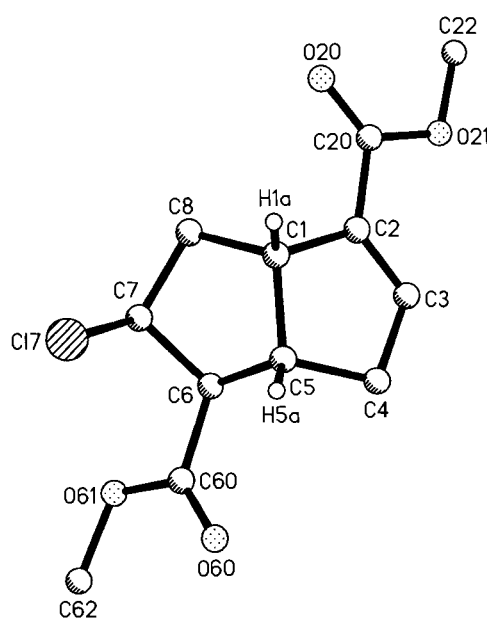

Figure 2. Perspective drawings of the chloro diester *exo*-12 with the numeration of the atoms corresponding to Table 7

Table 2. Yields, melting points, and spectroscopic data of some bicyclo[3.3.0]octadiene derivatives and the semibullvalene-2,6-dicarboxylate **2b**. Except for the compounds **9** and **10**, the reported yields were obtained after flash chromatography

Cpd.	Yield [%]	M.p. [°C]	IR [cm^{-1}] (KBr) C=O	C=C
9	43 – 52 [90	108 – 109 110][22]	1670	1635[a]
10	97 – 99	oil	1718 1661[b]	
exo-**11**	28	159	1733	
7a, *endo*-**11** (1:1)	4	73 – 88	1734 1713	1625
exo-**12**	13	87 – 88	1731 1710	1623
endo-**12**, **13** (1:10)	4	oil	1740 1725	1615[c]
7a	84	108 – 109	1710	1625
7b	37	80 – 81	1712	1626
17	50 – 61 [45 – 55	173 173][7]		
18[d]	10	32 – 35	1717 1709	1623
19a	63	139 – 140	1724	1620
19b	77	85 – 86	1708	1625
2b	90	94 – 95	1706 1705	1571

[a] Recorded from a solution in tetrachloromethane, 10-mm Infrasil quartz cell: $\tilde{v}$ = 3240 cm^{-1} (broad). — [b] Recorded from a solution in tetrachloromethane, 0.5-mm KBr cell: 10-mm Infrasil quartz cell: $\tilde{v}$ = 3600, 3450 cm^{-1} (broad). — [c] Recorded from a solution in tetrachloromethane, 0.5-mm KBr cell. — [d] C≡N: $\tilde{v}$= 2216 cm^{-1}.

The sequence leading to the α,β-unsaturated ester **7a** can be envisaged, in principle, to be suitable for the synthesis of the homologous ester **7b** by degradation of the corresponding 1,5-methylated β-oxo ester. Difficulties arose, however, because methyl groups at the bridgeheads of the bicyclo[3.3.0]octane system severely encumber the other ring atoms. Several attempts at the decarbalkoxylation of the 1,5-methylated β-oxo ester[21] under the conditions optimized for **8** met with failure. Therefore, we resorted to the well-known α,β-unsaturated dinitrile **17** as the precursor to **7b**.

The dinitrile **17**, being the key intermediate on the route to the 2,6-dicyanosemibullvalene **1b**[5−7] and a nortriasterane[29], has been synthesized from 1,5-dimethylbicyclo[3.3.0]octane-2,6-dione[5,6] and, more recently, from the isomeric 3,7-dione **14** as well[7]. The drawback of the former, seemingly straightforward procedure is that only multi-step routes lead to the diketone precursor. The latter synthesis, starting from the readily available diketone **14**, has now been

improved and adapted to a 30-g scale. The first improvement involved the preparative acid-catalysed equilibration of the 1:1 mixture of the vinyl sulphides C_2- and C_S-**15** obtained from **14** and 4-chlorothiophenol in the presence of titanium tetrachloride and triethylamine[7]. Thus, a 73:27 ratio in favour of the only useful isomer C_2-**15** is achieved. This ratio is preserved in the oxidation step effecting the umpolung of the system (→ C_2- and C_S-**16**). Secondly, the chromatographic system that allows isolation of **17** from the complex mixture of nitriles, obtained from C_2- and C_S-**16** and potassium cyanide supported on aluminium oxide, has been scaled up such as to separate portions of 7−8 g of the crude product affording a total of 6−7 g of **17** in a single experiment.
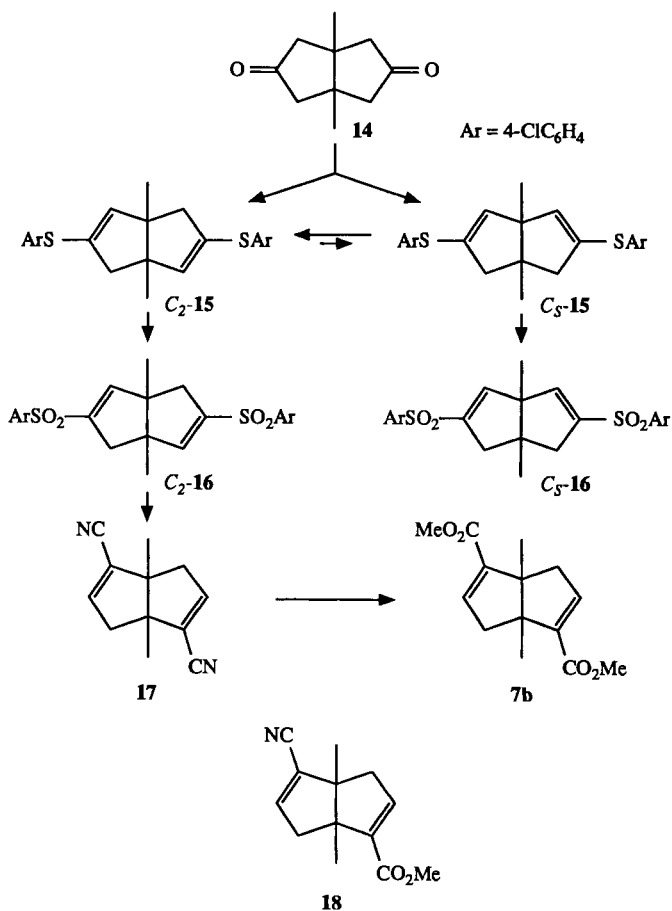
The dinitrile **17** turned out to be quite reluctant towards methanolysis, as expected on the basis of the encumbering vicinity of the cyano groups. Thus, a prolonged treatment of **17** with hot methanol in the presence of hydrochloric acid[30] followed by the hydrolysis of the intermediate Pinner salt resulted in an only modest yield of the diester **7b** besides some of the cyano ester **18** which was separated by flash chromatography (Table 2).

Both unsaturated esters **7a** and **b** were readily brominated at the allylic positions by *N*-bromosuccinimide in refluxing dichloromethane yielding the γ,γ'-dibromo diesters **19a** and **b** (Table 2). NMR spectroscopy indicated C_2 symmetry for **19a** and **b** as well (Tables 3 and 4). The *exo* configuration of the bromine atoms, which is a prerequisite to the reduc-

tive ring clos~~ ~~ording a semibullvalene, was confirmed ~~~ ~~a and **b** by X-ray diffraction analyses (Figure 3, Table 1).

Numerous examples attest to the usefulness of the zinc-copper couple for the reductive cyclization of bicyclo[3.3.0]octa-2,6-diene and bicyclo[3.3.1]nona-2,7-diene dibromides to semibullvalenes[5−7,11,14] and barbaralanes[3]. Therefore, it came as no surprise that the zinc-copper couple turned out to be the reagent of choice also for the cyclization of the dibromo diesters 19a and **b**. In refluxing tetrahydrofuran, both were converted into the corresponding semibullvalenes, 2a and **b**, in a smooth reaction as monitored by high-performance liquid chromatography. Though differing seemingly only very little, viz. by virtue of the substitution pattern at the bridgehead positions C1 and C5, the dimethyl semibullvalenedicarboxylates 2a and **b** showed a dramatic difference in their persistence in solution. While 2b was quite stable, to a certain extent even towards molecular oxygen, thus allowing convenient isolation and handling, the lower homologue 2a, devoid of bridgehead methyl groups, disappeared on concentration of its solutions, no matter how strictly molecular oxygen and moisture had been excluded. Most probably, the disappearance of 2a from more concentrated solutions is caused by a strong tendency to oligomerize or polymerize. This property has been reported for 1,5-dimethyl-3-phenyl-[13] and 1,5-dimethyl-3,7-diphenylsemibullvalene[31] and was recently found in the case of 2,6-dicyanosemibullvalene (1a)[11] which, like 2a, lacks the bridgehead methyl groups. Although the mechanism of the polymerization can only be speculated about in the absence of experimental evidence, the addition of a reactive species to the π acceptor-substituted semibullvalenes

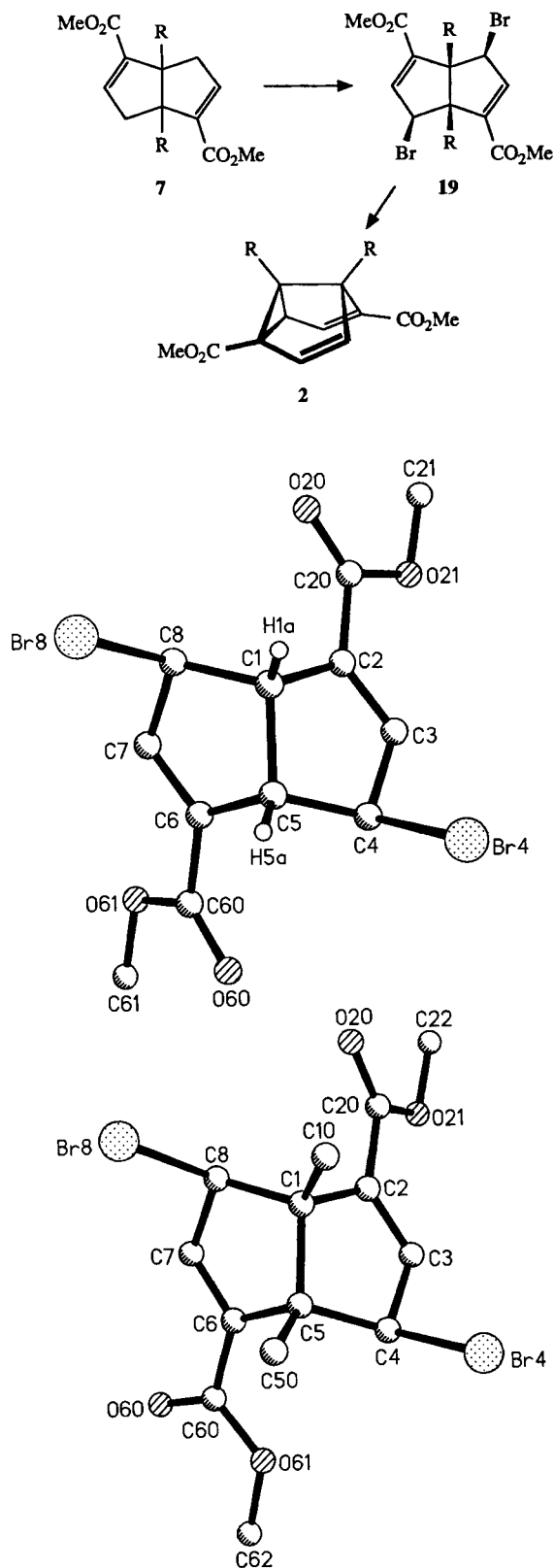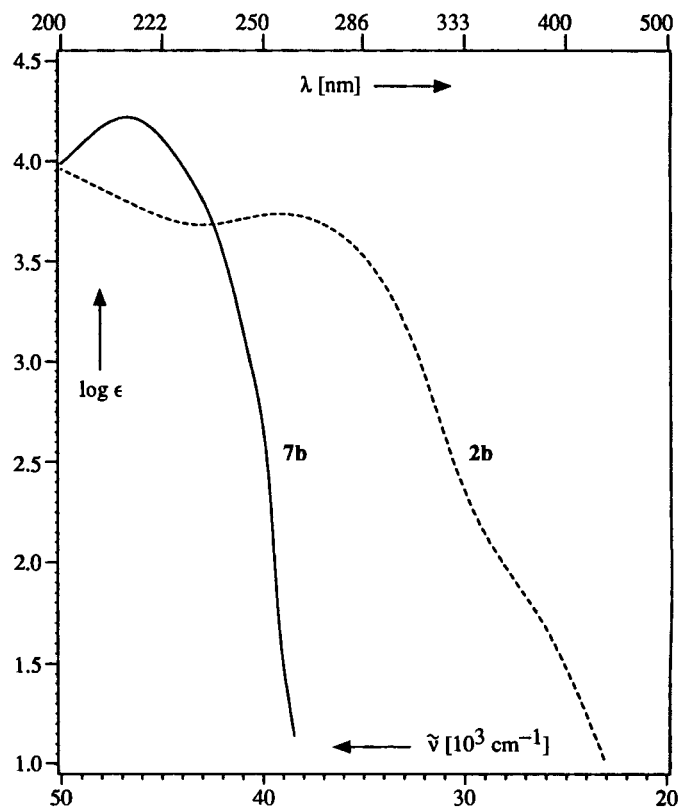Figure 3. Perspective drawings of the dibromo diesters 19a (above) and **b** (below) with the numeration of the atoms corresponding to Table 3 and 4

Figure 4. UV-spectra of the diester 7b and the semibullvalene 2b (solvent acetonitrile, 296 K)

1a and 2a with concomitant cleavage of the C2—C8 cyclopropane bond may well be the initial step. This hypothesis is corroborated by the tremendous increase in persistence when methyl groups are attached to the bridgehead atoms C1 and C5, as in 1b and 2b, because such methyl groups shield the double bond against addition reactions. Furthermore, when the cyano group of both 1a and b or the ester functionalities of 2a and b are formally replaced by phenylsulphonyl groups, significantly more persistent semibullvalenes result[32]. This observation may serve to support the hypothesis that, besides the lack of bridgehead substituents, the presence of π-conjugating groups is a prerequisite for the polymerization responsible for the disappearance of 1a and 2a. Be that as it may, 2a persisted long enough in solution to allow characterization by NMR spectroscopy, which left no room for any doubts about the structure, in particular when the data were compared to those of the homologue 2b. This was isolated after flash chromatography without any problems in 90% yield as lemon-coloured crystals melting at 94—95°C.

As in the case of the 2,6-dicyanosemibullvalene 1b, the dimethyl semibullvalenedicarboxylate 2b absorbs at a significantly longer wavelength (λ_{max} = 254 nm, Figure 4) than its precursor, viz. the bicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate 7b (λ_{max} = 215 nm, Figure 4). The yellow colour of 2b stems from a long-wavelength shoulder round 360 nm which closely resembles that of the 2,6-dicyanosemibullvalene 1b. The yellow crystals of 2b, and its solutions as well, become colourless on cooling, hence 2b exhibits reversible thermochromism like 1b which is independent of the liquid or solid state. Down to temperatures as low as −95°C, both dimethyl semibullvalenedicarboxylates 2a and b exhibit average NMR spectra in solution (Tables 3 and 4) which arise from equivalent, rapidly exchanging valence tautomers. A study of the degenerate Cope rearrangement and the reversible thermochromism will be reported elsewhere.

Experimental

Yields, melting points, and IR: Table 2. — ¹³C NMR: Table 3. — ¹H NMR: Tables 4—7, 9. — Molecular formulae and masses, and elemental analyses: Table 13. — Melting points: Sealed capillary tubes, Büchi, Flawil, Switzerland. — IR: Perkin-Elmer 1420. — ¹H NMR: Bruker AC 200 (19a 0.150 Hz/pt.), AC 250 (7b, 19b 0.305 Hz/pt.) and WM 400 (0.101 Hz/pt.). In order to resolve close signals and small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation[33]. Spectra of higher order were analysed by standard methods[34]. — ¹³C NMR: Bruker AC 200 and AC 250. — 70-eV MS: Finnigan MAT 8200. — UV: Hitachi U 3200, [ε] = [l mol⁻¹ cm⁻¹].

High-Performance Liquid Chromatography (HPLC): Chromatograph Waters M-6000A equipped with UV detector 440 (λ = 254 nm) and RI detector R401, (250 × 4.6) mm stainless steel column packed with LiChrosorb Si60, 5 μm (Merck), 1.5 ml/min petroleum ether (boiling range 50—70°C) (PE)/ethyl acetate (EA)

(95:5), retention times t_R [min] = 6.0 (2b), 7.0 (7b), 9.8 (19b), 10.0 (18), 18.2 (17); PE/EA (90:10), t_R = 10.4 (2a), 13.2 (7a), 16.0 (19a); PE/EA (80:20), t_R = 8.6 (7a, endo-11), 11.2 (endo-12, 13), 12.6 (exo-12), 30.4 (exo-11). — Chromatograph Bruker LC 21 A equipped with a UV detector Knauer No. 87.00 (λ = 254 nm) and an RI detector Erma ERC 7512, (250 × 4.6) mm stainless steel column packed with Nucleosil 100, 3 μm (Knauer), 2.0 ml/min PE/EA (90:10), t_R = 5.5 (17), 11.5 (16); PE/EA (80:20), t_R = 4.8 (7a, endo-11), 6.0 (endo-12, 13), 6.3 (exo-12), 14.5 (exo-11). — *Preparative Medium-Pressure Liquid Chromatography[27] with Automatic Recycling (MPLC)[28]:* UV detector Knauer No. 87.00 (λ = 254 nm) and RI detector Bischoff 8110, (70 × 7) cm glass column packed with LiChroprep Si60, 15—20 μm (Merck), 70 ml/min PE (30—50°C)/EA (80:20), 15 bar, t_R = 56 (7a), 57 (endo-11), 65—72 (17), 74 (endo-12, 13), 78 (exo-12), 134—150 (16). — *Flash Chromatography:* UV detector Knauer No. 87.00 (λ = 254 nm), (45 × 4) cm glass column packed with silica gel 32—63 μm (ICN-Biomedicals), PE/EA, 1.8 bar. — *Thin-Layer Chromatography (TLC):* Aluminium sheets precoated with silica gel 60 F_{254} (Merck).

Ether and tetrahydrofuran were distilled under Ar from sodium-potassium alloy. Dimethyl sulphoxide was distilled under vacuum from calcium hydride. Under N_2, 2-methyl-2-butanol and pyridine were distilled from calcium hydride, dichloromethane and trichloromethane from diphosphorus pentoxide, and methanol from magnesium methoxide. — Sodium hydride was freed from paraffin oil by repeated washings with PE (30—50°C) and dried in a stream of N_2. Phosphorus oxychloride was distilled under N_2 immediately before use. — The starting materials 8[21], 14[21] and potassium cyanide supported on basic aluminium oxide[7,35] have been prepared according to literature procedures. — The mixture of C_2- and C_S-15 (1:1)[7] was obtained after 24 h from 14 (0.30 mol in 0.7 l of tetrahydrofuran), titanium tetrachloride (0.63 mol), and a mixture of 4-chlorothiophenol (0.65 mol), triethylamine (1.26 mol), and tetrahydrofuran (0.5 l), kept at 45°C. Recrystallization of the crude product from ethanol (0.45 l) yielded pale yellow crystals (86%), m.p. 103—106°C (87—93%, 101—106°C[7]).

Acid-Catalysed Equilibration C_2-15 ⇌ C_S-15: Trifluoroacetic anhydride (3.6 ml, 26 mmol) and trifluoroacetic acid (1.1 ml, 14 mmol) were added to a solution of C_2- and C_S-15 (1:1, 106.6 g, 0.25 mol, recrystallized from ethanol) in trichloromethane (0.5 l). After stirring for 2 d, potassium carbonate (100 g, 0.73 mol) and a saturated aqueous solution of potassium carbonate (1 l) were added. The organic layer was extracted with water (0.5 l) and dried with potassium carbonate. Vacuum distillation of the solvent afforded pale yellow crystals of C_2- and C_S-15 (73:27, 103.7 g, 97%), m.p. 107—112°C (75:25, 91%, 102—117°C[7]).

3,7-Bis(4-chlorophenylsulphonyl)-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene (C_2-16) and 3,7-Bis(4-chlorophenylsulphonyl)-1,5-dimethylbicyclo[3.3.0]octa-2,7-diene (C_S-16): Oxidation of the mixture of C_2- and C_S-15 (73:27, 0.25 mol) with sodium perborate tetrahydrate (1.48 mol) in acetic acid (2.5 l) at 55°C was performed as described for the 1:1 mixture[7] yielding a colourless powder, m.p. 265—272°C (97%, C_2-/C_S-16 = 73:27, ¹H NMR) (Lit.[7] 81—94%, C_2-/C_S-16 = 75:25, m.p. 265—272°C).

Dimethyl 3,7-Dihydroxybicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (9): Methanol (200 ml, 6.25 mol) was added dropwise with stirring under N_2 to a suspension of sodium hydride (71.7 g, 2.50 mol) in dimethyl sulphoxide (1.5 l) while the temperature was kept at 20°C by cooling with ice/water. After the gas evolution had subsided, the colourless suspension was heated to 55°C, and 8 (46.6 g, 125 mmol) was added. Stirring at 55°C for 54 h gave rise to the formation of a colourless precipitate. — To the samples of

the reaction mixture (0.5 ml) was added 2 M hydrochloric acid (0.1 ml) and dichloromethane (0.5 ml), and the progress of the reaction was monitored by TLC with PE/acetone (7:3) containing formic acid (1%). The β-oxo esters **8** (R_f 0.37), **9** (R_f 0.57), and the inter-

Table 3. Chemical shifts (δ values) in carbon-13 NMR spectra of some bicyclo[3.3.0]octadienes and semibullvalenes recorded from [D]trichloromethane solutions. Chemical shifts of carbon-13 atoms that are equivalent in virtue of symmetry or a rapid degenerate Cope rearrangement are given only once

Cpd.	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	C=O	OMe	Me
7a	47.2	137.9	142.7	38.5	165.3	51.4	
	[47.2	137.9	142.6	38.6	165.3][18]		
7b	57.3	140.8	142.5	42.0	164.8	51.0	20.4
exo-**11**	41.7	58.4	64.9	42.2	170.5	52.3	
endo-**11**	41.3	58.7	64.3	41.5	170.5	52.03	
	44.5	59.7	60.4	42.9	172.7	52.27	
exo-**12**	47.3	138.3	141.8	37.7	164.9	51.4	
	40.8	58.6	63.3	42.4	170.8	52.0	
endo-**12**	47.0	138.4	141.1	38.2	164.6	51.4	
	40.8	58.3	60.3	41.8	173.0	52.0	
13	42.71	56.68	62.6	42.9	170.8	50.9	
	42.71	57.01	127.8	135.5	173.9	51.9	
18[a]	56.4	140.7	141.0	42.0	164.2	51.2	20.02
	58.8	123.0	145.5	42.8			20.16
19a[b]	52.7	137.1	141.6	58.2	163.4	51.5	
19b	60.9	141.0	142.1	59.6	164.2	52.3	20.3
Semibullvalenes							
2a[c]	55.0	98.6	125.7	95.1	164.7	51.4	
2b	66.1	101.1	125.3	99.4	167.8	51.7	12.1

[a] $C \equiv N$: δ = 115.8. — [b] Recorded from a solution in [D_6]benzene. — [c] Recorded from a solution in [D_8]tetrahydrofuran/[D_8]toluene (9:1).

Table 4. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton NMR spectra of some bicyclo[3.3.0]-octadienes and semibullvalenes recorded from [D]trichloromethane solutions. Chemical shifts of protons that are equivalent in virtue of symmetry or a rapid degenerate Cope rearrangement are given only once

Cpd.	1-H	3-H$_X$	4-H$_A$	4-H$_B$	OMe	Me	$^2J_{AB}$	$^3J_{AX}$	$^3J_{BX}$
2a[a,b]	3.48	5.85	4.70		3.65				4.1
2b		5.84	4.79		3.77	1.26			4.1
7a[b]	3.57	6.54	2.61	2.50	3.40		19.6	2.6	2.7
7b		6.67	2.99	2.29	3.68	1.21	19.3	2.1	3.1
19a[c]	4.12	6.42	4.88		3.34				2.6
19b		6.74	5.46		3.74	1.52			2.8

[a] Recorded from a solution in [D_8]tetrahydrofuran/[D_8]toluene (9:1). — [b] 400 MHz, 0.101 Hz/pt. — [c] Recorded from a solution in [D_6]benzene.

mediate triester (R_f 0.46) were detected with a solution of iron trichloride hexahydrate (1.0 g, 3.7 mmol) in a mixture of ethanol (200 ml), water (50 ml), and concentrated hydrochloric acid (2 ml). — The suspension was cooled to 20 °C and acidified to pH 4 with 4 M aqueous hydrochloric acid (0.8 l). The resulting orange-coloured solution was saturated with sodium chloride and continuously extracted with ether (2 l) for 8 h in a stirred extractor[36]. The ether solution was extracted with a saturated aqueous solution of sodium chloride (3 × 0.3 l) and dried with sodium sulphate. Vacuum distillation of the solvent and repeated recrystallization of the residue from ethanol yielded a colourless powder (16.3 g, 52%), m.p. 106—108 °C (Lit.[22] 90%, m.p. 110 °C, ^{13}C NMR).

Dimethyl 3,7-Dihydroxybicyclo[3.3.0]octane-2,6-dicarboxylate (**10**), *Mixture of Diastereomers:* A solution of hydrogen chloride in methanol (2.5 M, 180 ml, 450 mmol) was added dropwise with stirring under N_2 within 3.5 h to a suspension of **9** (18.5 g, 73 mmol) and $NaB(CN)H_3$ (11.3 g, 180 mmol) in methanol (250 ml), containing a small amount of methylorange as indicator, at such a rate that protonation of the indicator was maintained. After the gas evolution had subsided, a second portion (50 ml) of the 2.5 M hydrogen chloride solution in methanol was added. After stirring for 2 h, the solvent was distilled under vacuum and the oily, pink residue triturated with dichloromethane (150 ml). The colourless precipitate (sodium chloride) was filtered and washed with dichloromethane (50 ml). Vacuum distillation of the solvent afforded a pink oil (18.6 g, quant.), with slowly solidified. Attempts to separate the diastereomers by TLC on silica gel with trichloromethane/methanol (80:20, R_f 0.33) or by flash chromatography with EA or PE/EA (50:50) met with failure. The absence of β-oxo ester groups in the crude product, which was suitable for the next step, was proved by ^{13}C-NMR spectra. — ^{13}C NMR ([D]trichloromethane): δ = 39.3, 40.4, 40.6, 41.0, 41.2, 41.7, 42.2 (CH, CH_2), 50.8, 51.5, 51.7 (OMe), 58.0, 58.3, 58.5 (CH—CO_2Me), 75.1, 75.7, 76.5 (CHOH), 173.5, 173.7, 174.6 (C=O).

Reaction of **10** *with Phosphorus Oxychloride and Pyridine* (→ **7a**, *exo*-**11**, *endo*-**11**, *exo*-**12**, *endo*-**12**, **13**): Phosphorus oxychloride

Table 5. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton NMR spectra (400 MHz) of *endo*-**11** recorded from a solution in [D]trichloromethane[a]

	1-H	2-H	3-H	4-H$_x$	4-H$_n$	5-H	6-H	7-H	8-H$_x$	8-H$_n$
1-H	[b]	8.7							7.1	8.2
2-H			3.14	3.9						
3-H				4.75	2.0	4.5				
4-H$_{exo}$					2.49	14.1	8.2			
4-H$_{endo}$						2.19	8.3			
5-H						[b]	8.3			
6-H								2.75	8.0	
7-H									4.46	8.7	6.4
8-H$_{exo}$										1.76	13.6
8-H$_{endo}$											2.68

[a] OMe: δ = 3.74, 3.75. — [b] Hidden under the signals of the methoxy groups.

(12.3 g, 80 mmol) was added dropwise with stirring under N_2 at 0 °C within 10 min to a solution of **10** (5.17 g, 20 mmol) in pyridine (125 ml). The mixture was heated to 70 °C for 2 h. Vacuum distillation (10^{-2} Torr) of the solvent yielded a brown-black, viscous residue which was dissolved in dichloromethane (200 ml). Aqueous sulphuric acid (2 M, 70 ml) was added cautiously at 0 °C. The organic layer was extracted with aqueous sulphuric acid (2 M, 3 × 50 ml) which was reextracted with dichloromethane (2 × 50 ml). Drying with sodium sulphate and vacuum distillation of the solvent produced a brown oil (3.7 g) which was separated into 3 fractions (A, B, C) by flash chromatography with PE/EA (80:20). — Attempts to separate fraction A by MPLC failed. As many as 7 recycling steps afforded only a colourless solid (166 mg, 4%, melting range 73−88 °C) which consisted of **7a** and *endo*-**11** in equal proportions (^{1}H NMR).

Fraction B consisted largely of two components (HPLC). After three passages through the MPLC column, a colourless oil (200 mg,

4%) was obtained which was shown by ^{1}H NMR to be a mixture of *endo*-**12** and **13** (1:10). The second MPLC fraction yielded a colourless powder (650 mg, 13%, m.p. 85−87 °C). Recrystallization from PE/dichloromethane (1:1) furnished *exo*-**12** as colourless crystals, m.p. 88−89 °C. — MS: m/z (%) = 260, 258 (3, 9) [M$^+$], 228, 226 (26, 73) [M$^+$ − MeOH], 163 (67), 162 (65), 103 (100), 77 (48), 59 (46).

On recrystallization from PE/dichloromethane (1:1), fraction C yielded *exo*-**11** as colourless crystals (1.66 g, 28%), m.p. 159 °C. — MS: m/z (%) = 267, 265, 263 (2, 11, 16) [M$^+$ − OMe], 261, 259 (15, 44) [M$^+$ − Cl], 222 (42) [M$^+$ − 2 HCl], 201, 199 (12, 35), 163 (82), 162 (100), 105 (63), 59 (43).

Table 6. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton NMR spectra (400 MHz) of **13** recorded from a solution in [D]trichloromethane[a]

	1-H	2-H	3-H	4-H$_x$	4-H$_n$	5-H	6-H	7-H	8-H
1-H	3.33	7.5						2.2	2.4
2-H		2.85	4.2						
3-H			4.62		4.2				
4-H$_{exo}$				2.53	13.5	8.1			
4-H$_{endo}$					1.83	9.0			
5-H							3.46		
6-H								3.88	
7-H								5.66	5.5
8-H									5.86

[a] OMe: δ = 3.71, 3.76.

Table 7. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton NMR spectra (400 MHz) of *exo*-**12** recorded from a solution in [D]trichloromethane[a]

	1-H	3-H	4-H$_x$	4-H$_n$	5-H	6-H	7-H	8-H$_x$	8-H$_n$
1-H	[b]		2.2	2.8				8.6	7.6
3-H		6.63	2.4	2.8					
4-H$_{exo}$			2.87	19.7	9.2				
4-H$_{endo}$				2.33	2.8				
5-H					3.44	9.8			
6-H						2.80	4.2		
7-H							4.64	1.4	4.7
8-H$_{exo}$								2.63	14.7
8-H$_{endo}$									1.96

[a] OMe: δ = 3.74, 3.75. — [b] Hidden under the signals of the methoxy groups.

Table 8. Atomic parameters (× 10^4) ans isotropic thermal displacement parameters U_{equiv} (× 10^{-1}) [pm^2] for the dichloro diester *exo*-**12**. The parameters U_{equiv} are defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Cl(3)	6379	3959(1)	3941	60(1)
Cl(7)	5163(1)	8738(2)	9453(1)	63(1)
C(1)	5657(3)	8053(5)	5839(3)	42(1)
C(2)	5812(3)	8073(5)	4096(4)	43(1)
C(3)	5375(3)	5989(5)	3507(4)	46(1)
C(4)	4378(3)	5644(6)	4457(4)	51(1)
C(5)	4744(3)	6421(5)	6070(4)	43(1)
C(6)	3851(3)	7521(5)	6938(4)	45(1)
C(7)	4423(3)	9426(5)	7685(4)	48(1)
C(8)	5218(3)	10089(5)	6498(4)	51(1)
C(20)	6965(3)	8581(5)	3639(4)	44(1)
O(20)	7706(2)	9161(5)	4489(3)	62(1)
O(21)	7042(2)	8351(5)	2140(3)	64(1)
C(22)	8074(4)	8855(7)	1520(5)	73(2)
C(60)	3269(3)	6183(5)	8048(4)	53(1)
O(60)	3475(3)	4407(5)	8330(4)	97(2)
O(61)	2470(2)	7232(4)	8669(3)	62(1)
C(62)	1852(4)	6144(7)	9786(6)	86(2)

Table 9. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton NMR spectra (400 MHz) of *exo*-**11** recorded from a solution in [D]trichloromethane[a]. Chemical shifts of protons that are equivalent in virtue of symmetry are given only once

	1-H	2-H	3-H	4-H$_{exo}$	4-H$_{endo}$
1-H	3.53				
2-H		2.88	4.2		
3-H			4.71	2.0	4.5
4-H$_{exo}$				2.54	13.9
4-H$_{endo}$					1.87

[a] OMe: δ = 3.75.

Dimethyl Bicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (**7a**): Reduction of **9** (17.5 g, 69 mmol), as described above, yielded **10** (16.8 g, 98%) as an oil which was treated with phosphorus oxychloride (29.9 g, 195 mmol) and pyridine (275 ml) to afford a brown oil (9.5 g) consisting mainly of **7a**, *exo*-**11**, *endo*-**11**, *exo*-**12**, *endo*-**12** and **13** (HPLC). The oil was dissolved in dichloromethane (75 ml) and the solution filtered through silica gel (40 g, 32−63 μm) which was eluted with dichloromethane (250 ml). The clear yellow solu-

Table 10. Atomic parameters ($\times 10^4$) and equivalent isotropic displacement parameters U_{equiv} ($\times 10^{-1}$) [pm²], as defined in Table 8, for the chloro diester exo-11

	x	y	z	U_{eq}
Cl(7)	2274(1)	314(1)	1572(1)	65(1)
C(1)	3730(1)	563(3)	4253(5)	54(1)
C(2)	4262(1)	969(3)	5892(5)	59(1)
C(3)	4215(2)	345(4)	7749(6)	71(1)
C(4)	3660(2)	-659(4)	7733(6)	70(1)
C(5)	3280(2)	-355(3)	5585(5)	56(1)
C(6)	2661(1)	516(3)	5802(4)	48(1)
C(7)	2601(1)	1376(3)	3761(5)	51(1)
C(8)	3304(1)	1777(3)	3371(5)	57(1)
C(20)	4766(2)	2002(4)	5335(6)	66(1)
O(20)	4783(1)	2581(3)	3668(5)	87(1)
O(21)	5193(1)	2214(3)	7011(4)	85(1)
C(22)	5692(2)	3215(5)	6675(7)	94(2)
C(60)	2064(2)	-332(3)	6288(5)	55(1)
O(60)	2063(1)	-1516(2)	6723(4)	75(1)
O(61)	1524(1)	465(2)	6178(4)	66(1)
C(62)	922(2)	-261(5)	6542(7)	89(2)

tion was concentrated under vacuum to 30 ml. A solution of sodium (1.15 g, 50 mmol) in methanol (100 ml) was added under N₂. The yellow suspension was stirred for 1.5 h, cooled to 0°C, and acidified with 2 M sulphuric acid (20 ml, 40 mmol). After addition of dichloromethane (50 ml) and water (80 ml), the aqueous phase was extracted with dichloromethane (3 × 50 ml). The combined organic layers were extracted with a saturated aqueous solution of sodium chloride (2 × 40 ml) and dried with sodium sulphate. Vacuum distillation of the solvent afforded a beige powder (6.6 g) which, after flash chromatography with PE/EA (90:10), yielded colourless crystals (5.7 g, 76%), m.p. 108−109°C (111°C[18]) and a light brown powder (0.67 g). Recrystallization of the powder from PE/EA (1:1) furnished colourless crystals (0.58 g, 8%), m.p. 107−108°C. − MS: m/z (%) = 222 (88) [M⁺], 190 (100) [M⁺ − MeOH], 162 (83), 103 (88), 77 (37), 59 (29).

1,5-Dimethylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarbonitrile (17): A 4-l three-necked flask equipped with a heavy-duty stainless steel stirrer (Juchheim, W-5550 Bernkastel-Kues) and a reflux condenser protected by a drying tube was charged with a mixture of C_2- and C_S-16 (73:27, 58.0 g, 0.12 mol), potassium cyanide supported on aluminium oxide (370 g, 0.1 g KCN/g, 0.57 mol KCN) and 2-methyl-2-butanol (1.4 l). The suspension was stirred and heated under reflux for 60 h, while the conversion was monitored by HPLC. After cooling to 20−25°C, the solid material was filtered and washed with dichloromethane (5 × 0.4 l). The filtrate was extracted with an aqueous solution of sodium chloride in water (10%, 3 × 12 l) and dried with sodium sulphate. After vacuum distillation (15→10⁻² Torr) of the solvent, the solid dark-brown residue was dissolved in dichloromethane (0.2 l). The solution was filtered through a pad of silica gel (80 g, 32−63 μm) which was eluted with dichloromethane (0.5 l). Distillation of the solvent yielded a brown solid (28−34 g). On MPLC of four portions (7.5−8.0 g dissolved in dichloromethane, 15−25 ml), 17 (6.0−7.1 g, 50−61%), m.p. 171−173°C, was eluted as the first fraction. The pale yellow crystals were sublimed at 80°C bath temp./5 · 10⁻² Torr to furnish colourless crystals, m.p. 173°C (173°C[17]). From five experiments employing 224 g of C_2- and C_S-16 (73:27, 0.464 mol), a total of 32.5 g (52%) of 17 was obtained after sublimation.

Dimethyl 1,5-Dimethylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (7b) *and Methyl 6-Cyano-1,5-dimethylbicyclo[3.3.0]octa-2,6-*

diene-2-carboxylate (18): A solution of 17 (4.46 g, 24 mmol) in methanol (150 ml) was saturated with dry hydrogen chloride and heated under reflux, while the conversion was monitored by HPLC. Every 24 h, methanol (20−40 ml) was added, and the colourless solution was saturated again with hydrogen chloride. After 80−90% conversion of 18 (5−6 d), concentrated hydrochloric acid (50 ml), water (50 ml), and dichloromethane (150 ml) were added to the pale yellow solution at 20−25°C, and the mixture was stirred for 4 h. The aqueous layer was extracted with dichloromethane (3 × 70 ml). The combined organic layers were extracted with a saturated aqueous solution of sodium hydrogen carbonate (2 × 50 ml) and dried with sodium sulphate. Vacuum distillation of the solvent afforded a brown oil (2.9−3.4 g) which, on flash chromatography with PE/EA (96:4), yielded 7b (1.46−2.10 g, 29−35%) as colourless crystals, m.p. 80−81°C, and 18 (0.44−0.49 g, 8−10%) as a colourless powder, m.p. 35−39°C. − 7b: UV (acetonitrile, Figure 4): λmax [nm] (lg ε) = 215 (4.228). − MS: m/z (%) = 250 (38) [M⁺], 218 (100) [M⁺ − MeOH], 203 (20) [M⁺ − MeOH − Me], 190 (20), 186 (14), 159 (36), 158 (15), 131 (41).

Dimethyl exo,exo-4,8-Dibromobicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (19a): A mixture of 7a (2.20 g, 10 mmol), N-bromosuccinimide (3.78 g, 22 mmol), and dichloromethane (125 ml) was heated under reflux and stirring, and irridiated with a 250-W daylight lamp (Philips ML), while the conversion was monitored by HPLC. After 7.5 h, the solution was allowed to cool to 20−25°C, extracted with an aqueous solution of sodium hydroxide (0.5 M, 2 × 70 ml) and a saturated aqueous solution of sodium chloride (2 × 80 ml), and dried with sodium sulphate. Vacuum distillation of the solvent afforded a solid, orange-red residue which yielded a colourless powder after flash chromatography with PE/EA (95:5). Colourless crystals crystallized from dichloromethane (2.31 g, 62%), m.p. 139−140°C. − MS: m/z (%) = 382, 380, 378 (5, 10, 5) [M⁺], 301, 299 (97, 100) [M⁺ − Br], 220 (40) [M⁺ − 2 Br], 219 (57) [M⁺ − HBr − Br], 160 (40), 102 (45), 59 (32).

Table 11. Atomic parameters ($\times 10^4$) and equivalent isotropic displacement parameters U_{equiv} ($\times 10^{-1}$) [pm²], as defined in Table 8, for the dibromo diester 19a

	x	y	z	U_{eq}
Br(4)	5472(1)	-764(1)	-2781(1)	64(1)
Br(8)	9008(1)	946(1)	1220(1)	64(1)
C(1)	7417(4)	1253(6)	-1227(6)	41(2)
C(2)	6853(4)	2195(6)	-2409(7)	41(2)
C(3)	6342(4)	1519(6)	-3553(7)	46(2)
C(4)	6491(4)	5(6)	-3365(7)	45(2)
C(5)	7340(4)	-140(6)	-2111(6)	39(2)
C(6)	8163(4)	-117(6)	-2627(7)	41(2)
C(7)	8742(4)	813(6)	-1929(6)	47(2)
C(8)	8400(4)	1610(6)	-837(6)	46(2)
C(20)	6875(5)	3689(6)	-2175(7)	46(2)
O(20)	7288(3)	4258(4)	-1075(5)	64(2)
O(21)	6373(3)	4338(4)	-3388(5)	55(2)
C(21)	6347(6)	5826(6)	-3288(8)	75(4)
C(60)	8304(5)	-1099(6)	-3766(7)	44(2)
O(60)	7841(3)	-2075(4)	-4189(5)	61(2)
O(61)	9020(3)	-784(4)	-4217(5)	58(2)
C(61)	9203(6)	-1683(7)	-5336(8)	76(4)

Dimethyl exo,exo-4,8-Dibromo-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (19b): According to the procedure described for 19a, an orange-coloured solution was obtained after 1.5 h from a mixture of 7b (1.00 g, 4.0 mmol), N-bromosuccinimide

(1.66 g, 9.3 mmol), and dichloromethane (150 ml). Work-up as described yielded a pale brown powder which furnished colourless crystals (1.25 g, 77%), m.p. 85–86°C, after flash chromatography with PE/EA (94:6). — MS: m/z (%) = 410, 408, 406 (18, 37, 18) [M$^+$], 329, 327 (83, 86) [M$^+$ – Br], 297, 295 (99, 100) [M$^+$ – Br – MeOH], 248 (42) [M$^+$ – 2 Br], 216 (56), 188 (63), 157 (41), 129 (79).

Table 12. Atomic parameters ($\times 10^4$) and equivalent isotropic displacement parameters U_{equiv} ($\times 10^{-1}$) [pm^2], as defined in Table 8, for the dibromo diester **19b**

	x	y	z	U_{eq}
Br(4)	2789(1)	2205(1)	1606(1)	67(1)
Br(8)	6756(1)	936(1)	815(1)	71(1)
C(1)	5173(3)	1958(3)	863(5)	35(2)
C(2)	4953(3)	2736(3)	480(5)	37(2)
C(3)	4104(3)	2814(3)	127(5)	44(2)
C(4)	3591(3)	2117(3)	207(5)	45(2)
C(5)	4339(3)	1518(3)	363(5)	38(2)
C(6)	4690(3)	1297(3)	-840(5)	39(2)
C(7)	5575(3)	1395(3)	-950(5)	48(2)
C(8)	5984(3)	1701(3)	120(5)	44(2)
C(10)	5302(4)	1916(3)	2188(5)	52(2)
C(20)	5645(4)	3329(3)	540(5)	42(2)
O(20)	6329(3)	3284(2)	1097(4)	61(2)
O(21)	5403(3)	3907(2)	-98(4)	57(2)
C(22)	6024(4)	4519(3)	-75(7)	80(3)
C(50)	4066(4)	834(3)	1072(5)	53(2)
C(60)	4171(4)	963(3)	-1820(5)	48(2)
O(60)	4509(3)	738(3)	-2699(4)	73(2)
O(61)	3288(2)	941(2)	-1618(3)	53(1)
C(62)	2727(4)	659(3)	-2541(6)	69(3)

Dimethyl Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene-2,6-dicarboxylate (**2a**): On a high-vacuum line, a suspension of a small amount of sodium hydride in a mixture of [D$_8$]tetrahydrofuran (0.9 ml), [D$_8$]toluene (0.1 ml), and one drop of tetramethylsilane was stirred under Ar for 24 h and carefully degassed at 10^{-5} Torr (3×). Under Ar, a (6 × 1) cm glass tube, equipped with a small glass sinter filter, which was connected to an NMR sample tube, was charged with zinc-copper couple (65 mg, 0.54 mmol) and **19a** (95 mg, 0.25 mmol) and evacuated to 10^{-5} Torr. Under high vacuum, the solvent mixture (0.7 ml) was transferred into the glass tube which was cooled with liquid N$_2$. The apparatus was flame-sealed at 10^{-5} Torr and heated to 70°C for 10 min. The suspension was allowed to cool to 20–25°C and filtered to yield a clear, yellow solution, which was sealed in the NMR sample tube. The NMR spectra indicated a complete conversion of **19a** to **2a**. Numerous attempts to isolate **2a** by concentrating solutions prepared similarly gave rise to the disappearance of **2a** as monitored by NMR and HPLC.

Dimethyl 1,5-Dimethyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene-2,6-dicarboxylate (**2b**): A mixture of **19b** (1.11 g, 2.7 mmol), zinc-copper couple (2.50 g, 19.4 mmol), and tetrahydrofuran (30 ml) was heated under Ar and reflux for 20 min, while the conversion was monitored by HPLC. The mixture was filtered through silica gel (50 g, 32–63 μm) which was eluted with dichloromethane (70 ml). Drying with sodium sulphate and vacuum distillation of the solvent afforded a solid which yielded lemon-coloured crystals (0.61 g, 90%), m.p. 94–95°C, after flash chromatography with PE/EA (90:10). — UV (acetonitrile, Figure 4): λ_{max} [nm] (lg ε) = 254 (3.775), 355 (sh) (1.977); λ_{min} [nm] (lg ε) = 233 (3.604). — MS: m/z = 248 (72) [M$^+$], 216 (79) [M$^+$ – MeOH], 189 (86) [M$^+$ – CO$_2$Me], 188 (90), 157 (74), 129 (100), 128 (39).

Table 13. Molecular formulae, masses and elemental analyses for some bicyclo[3.3.0]octadienes and the semibullvalene-2,6-dicarboxylate **2b**

Cpd.		Molecular Mass	Elemental Analysis			
				C	H	N
2b	C$_{14}$H$_{16}$O$_4$	248.3	Calcd.	67.73	6.50	
			Found	68.05	6.67	
7a	C$_{12}$H$_{14}$O$_4$	222.2	Calcd.	64.85	6.35	
			Found	64.86	6.48	
7b	C$_{14}$H$_{18}$O$_4$	250.3	Calcd.	67.18	7.25	
			Found	67.43	7.44	
exo-**11**	C$_{12}$H$_{16}$Cl$_2$O$_4$	295.2	Calcd.	48.83	5.46	
			Found	49.12	5.59	
exo-**12**	C$_{12}$H$_{15}$ClO$_4$	258.7	Calcd.	55.71	5.84	
			Found	56.02	5.91	
endo-**12, 13**[a]	C$_{12}$H$_{15}$ClO$_4$		Found	55.93	5.94	
18	C$_{13}$H$_{15}$NO$_2$	217.3	Calcd.	71.87	6.96	6.45
			Found	71.89	6.98	6.89
19a	C$_{12}$H$_{12}$Br$_2$O$_4$	380.0	Calcd.	37.93	3.18	
			Found	38.10	3.17	
19b	C$_{14}$H$_{16}$Br$_2$O$_4$	408.1	Calcd.	41.20	3.95	
			Found	41.49	4.00	

[a] *endo*-**12**: **13** = 1:10.

X-Ray Diffraction Analyses were performed from colourless, transparent crystals. The cell parameters were determined on the basis of 22 reflections. The numbers of reflections reported in Table 1 were obtained with Mo-K_α radiation and $2\Theta_{max}$ = 55° (graphite monochromator, Wyckoff scan). Measurements were carried out with the system Nicolet R3m/V. Computations were performed on a computer Micro-Vax II. The programme SHELXTL-PLUS[37] was employed. The structures were solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is 1/σ^2. The positions of hydrogen atoms were calculated and included in the refinements with isotropic description[38].

[1] The results are part of the projected Dissertation by A. Witzel, Universität Würzburg.

[2] R. Hoffmann, W.-D. Stohrer, *J. Am. Chem. Soc.* **1971**, *93*, 6941–6953; M. J. S. Dewar, D. H. Lo, *ibid.* **1971**, *93*, 7201–7207; M. J. S. Dewar, Z. Náhlovská, B. D. Náhlovský, *J. Chem. Soc., Chem.Commun.* **1971**, 1377–1378; M. J. S. Dewar, C. Jie, *Tetrahedron* **1988**, *44*, 1351–1358; L. S. Miller, K. Grohmann, J. J. Dannenberg, *J. Am. Chem. Soc.* **1983**, *105*, 6862–6865.

[3] H. Quast, Y. Görlach, J. Stawitz, *Angew. Chem.* **1981**, *93*, 96–98; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 93–94; H. Quast, Y. Görlach, J. Stawitz, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1984**, *117*, 2745–2760.

[4] L. M. Jackman, G. Ibar, A. J. Freyer, Y. Görlach, H. Quast, *Chem. Ber.* **1984**, *117*, 1671–1678.

[5] [5a] R. Askani, M. Littmann, *Tetrahedron Lett.* **1982**, *23*, 3651–3652. — [5b] H. Quast, J. Christ, Y. Görlach, W. von der Saal, *Tetrahedron Lett.* **1982**, *23*, 3653–3656.

[6] H. Quast, J. Christ, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1985**, *118*, 1154–1175.

[7] H. Quast, A. Mayer, *Liebigs Ann. Chem.* **1988**, 1155–1163.

[8] H. Quast, J. Christ, *Angew. Chem.* **1984**, *96*, 606−607; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 631−632.
[9] L. M. Jackman, A. Benesi, A. Mayer, H. Quast, E.-M. Peters, K. Peters, H. G. von Schnering, *J. Am. Chem. Soc.* **1989**, *111*, 1512−1513.
[10] H. Quast, A. Mayer, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1989**, *122*, 1291−1306.
[11] The 1,5-unsubstituted semibullvalene-2,6-dicarbonitrile (**1a**) behaves similarly, but exact measurements were precluded by its lack of persistence: H. Quast, R. Janiak, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 969−973.
[12] I. Sellner, H. Schuster, H. Sichert, J. Sauer, H. Nöth, *Chem. Ber.* **1983**, *116*, 3751−3761.
[13] C. Schnieders, K. Müllen, C. Braig, H. Schuster, J. Sauer, *Tetrahedron Lett.* **1984**, *25*, 749−752.
[14] H. Quast, Y. Görlach, E.-M. Peters, K. Peters, H. G. von Schnering, L. M. Jackman, G. Ibar, A. J. Freyer, *Chem. Ber.* **1986**, *119*, 1801−1835.
[15] D. Paske, R. Ringshandl, I. Sellner, H. Sichert, J. Sauer, *Angew. Chem.* **1980**, *92*, 464−465; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 456−457; H. Schuster, H. Sichert, J. Sauer, *Tetrahedron Lett.* **1983**, *24*, 1485−1488.
[16] L. S. Miller, K. Grohmann, J. J. Dannenberg, L. Todaro, *J. Am. Chem. Soc.* **1981**, *103*, 6249−6251.
[17] R. Askani, *Tetrahedron Lett.* **1971**, 447−450.
[18] M. J. Goldstein, T. T. Wenzel, G. Whittaker, S. F. Yates, *J. Am. Chem. Soc.* **1982**, *104*, 2669−2671.
[19] U. Weiss, J. M. Edwards, *Tetrahedron Lett.* **1968**, 4885−4887.
[20] For reviews of the Weiss reaction see: M. Ramaiah, *Synthesis* **1984**, 529−570; H.-U. Reissig in *Organic Synthesis Highlights* (Eds.: J. Mulzer, H.-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig), 1st ed., VCH-Verlagsgesellschaft, Weinheim, **1991**, p. 121−125; A. K. Gupta, X. Fu, J. P. Snyder, J. M. Cook, *Tetrahedron* **1991**, *47*, 3665−3710.
[21] S. H. Bertz, J. M. Cook, A. Gawish, U. Weiss, *Org. Synth., Coll. Vol.* **1990**, *7*, 50−56.
[22] S. P. Bhatnagar, U. Weiss, R. J. Highet, *J. Org. Chem.* **1977**, *42*, 3089−3091.
[23] E. Jaeger, J. H. Biel, *J. Org. Chem.* **1965**, *30*, 740−744.
[24] W. Flitsch, F.-J. Lüttig, K. Rutkowski, *Chem. Ber.* **1987**, *120*, 1925−1932.

[25] J. Domagala, J. Wemple, *Tetrahedron Lett.* **1973**, 1179−1182.
[26] R. P. Graber, A. C. Haven, Jr., N. L. Wendler, *J. Am. Chem. Soc.* **1953**, *75*, 4722−4724; C. W. Shoppee, G. H. R. Summers, *J. Chem. Soc.* **1952**, 1786−1790; E. M. Chamberlin, E. W. Tristram, T. Utne, J. M. Chemerda, *J. Org. Chem.* **1960**, *25*, 295−297.
[27] G. Helmchen, B. Glatz, *Ein apparativ einfaches System und Säulen höchster Trennleistung zur präparativen Mitteldruck-Flüssigkeitschromatographie*, Universität Stuttgart, **1978**; E. Ade, G. Helmchen, G. Heiligenmann, *Tetrahedron Lett.* **1980**, *21*, 1137−1140.
[28] B. A. Bidlingmeyer, *Preparative Liquid Chromatography* (Journal of Chromatography Library, vol. 38), 1st ed., Elsevier, Amsterdam, **1987**; A. Werner, *Kontakte (Darmstadt)* **1989**, *3*, 50−56; H. Quast, H. Jakobi, B. Seiferling, *Liebigs Ann. Chem.* **1991**, 41−46.
[29] H. Quast, J. Christ, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1985**, *118*, 1176−1182.
[30] W. Betz, J. Daub, *Chem. Ber.* **1972**, *105*, 1778−1779; H. Henecka, *Methoden Org. Chem. (Houben-Weyl)*, 4th ed. **1952**, vol. 8/3, p. 536.
[31] R. Askani, R. Kirsten, B. Dugall, *Tetrahedron* **1981**, *37*, 4437−4444.
[32] H. Quast, J. Carlsen, R. Janiak, E.-M. Peters, K. Peters, H. G. von Schnering, *Chem. Ber.* **1992**, *125*, 955−968.
[33] A. E. Derome, *Modern NMR Techniques for Chemistry Research*, 1st ed., Pergamon Press, Oxford, **1987**.
[34] H. Günther, *NMR Spektroskopie*, 3rd ed., Thieme, Stuttgart, **1992**.
[35] J. H. Clark, C. V. A. Duke, *J. Org. Chem.* **1985**, *50*, 1330−1332.
[36] J. H. Choney, M. W. Adkins, E. J. Eisenbraun, *J. Chem. Educ.* **1987**, 970.
[37] G. M. Sheldrick, Universität Göttingen, unpublished.
[38] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56121, the names of the authors, and the journal citation.

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