232. ^{1}H-NMR Spectra of Cyclohexa-1,4-dienes and Cyclohexenes Annellated to Bicyclo[2.2.1]hept-2-enes. The Inter-Ring Homoallylic H,H Coupling Constants as Stereochemical Probes

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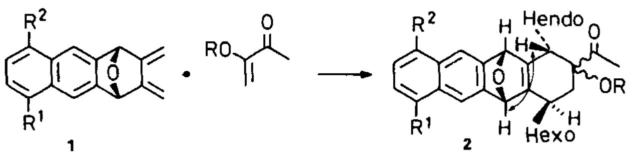
Dedicated to Prof. Dr. *Tino Gäumann* on the occasion of his 60th birthday

(10.V.85)

The 360-MHz-^{1}H-NMR spectra of cyclohexa-1,4-dienes and cyclohexenes annellated to bicyclo[2.2.1]hept-2-enes and 7-oxabicyclo[2.2.1]hept-2-enes show inter-ring homoallylic coupling constants between the bridgehead protons of the bicyclo[2.2.1]heptenes and the *exo*-protons of the allylic methylene groups (0.8 ± 0.15 Hz for bicyclo[2.2.1]hept-2-enes; 0.8–1.4 Hz for 7-oxabicyclo[2.2.1]hept-2-enes). Contrastingly, the corresponding coupling between the bridgehead protons and the *endo*-protons is absent. The observed values are compared with those calculated by the INDO and CNDO/2 methods and discussed in the light of the bicyclo[2.2.1]hept-2-ene bond π-anisotropy. Vicinal as well as intra-ring homoallylic coupling constants are consistent with a small puckering of the cyclohexa-1,4-diene rings toward the *endo*-face. The allylic *exo*-methylene protons are more deshielded than the *endo*-protons independent of the nature of the substituents, the nature of the bridges, and the degree of unsaturation of the annellated systems. These results constitute a probe for the configuration of cyclohexa-1,4-dienes and cyclohexenes annellated to these bicyclic skeletons.

Introduction. – In the course of our studies on the synthesis of anthracyclines [1–4] based on the *Diels-Alder* additions of exocyclic s-*cis*-butadiene moieties grafted onto 7-oxabicyclo[2.2.1]heptane derivatives **1**, we observed ^{1}H-NMR spectra of the corresponding adducts **2** with measurable homoallylic ^5J(H,H) coupling constants of *ca.* 1 Hz between the bridgehead protons of the 7-oxabicyclo[2.2.1]heptene systems and the allylic protons of the annellated cyclohexene moieties [3–5]. This was true for the *exo*-protons only; no such long-range coupling could be detected for the *endo*-allylic protons. In order to determine whether this feature could be taken as a probe for the configuration of the *Diels-Alder* adducts **2**, we prepared a series of cyclohexenes and cyclohexa-1,4-dienes annellated to various bicyclo[2.2.1]hept-2-ene and 7-oxabicyclo[2.2.1]hept-2-ene skeletons. We report now on their high-field (360 MHz) ^{1}H-NMR properties and show that the inter-ring homoallylic ^5J(H,H) coupling constants indeed constitute the probe we were looking for.



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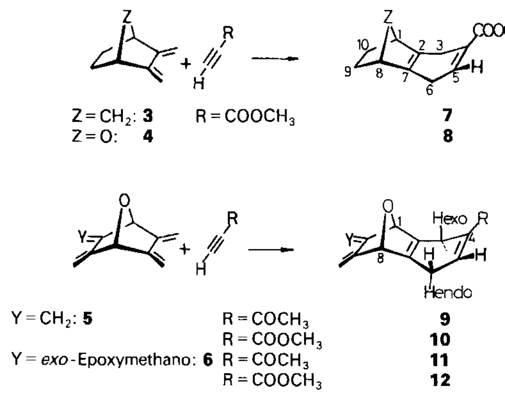
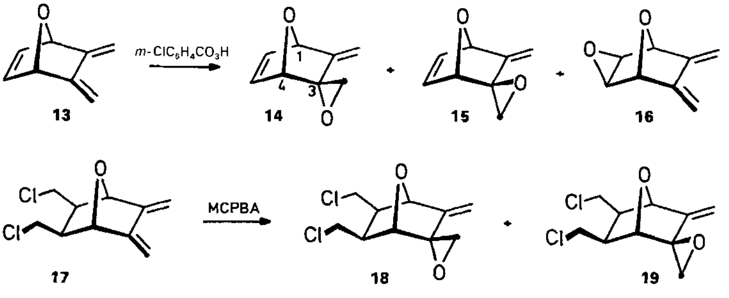
Scheme 1



Results. – The dienes **3** [6] and **4** [7], the tetraene **5** [8], and the epoxy-triene **6** added to methyl propynoate and 3-butyn-2-one and gave the corresponding cyclohexa-1,4-dienes **7**–**12** *(Scheme 1)* whose structure was ascertained by combustion analysis and their spectral data. The new epoxy-triene **6** [9] was obtained as major product in the mono-epoxidation of tetraene **5** in the presence of 1 mol-equiv. of *meta*-chloroperbenzoic acid (m-$ClC_6H_4CO_3H$) in CH_2Cl_2. The *Diels-Alder* additions of **6** were regioselective **11** and **12** being the major adducts with butynone and methyl propynoate, respectively [9]. The *exo*-configuration of the epoxides in **6**, **11**, and **12** was given by the ^{1}H-coupled ^{13}C-NMR spectra. No vicinal ^3J(C,H) coupling constant could be detected between the *exo*-epoxy C-atom (*exo* refers to the O-atom) and the adjacent bridgehead H-atom whereas, in the *endo*-isomers, a ^3J(C,H) of 3–5 Hz is generally observed. This is typical of bicyclo[2.2.1]heptane systems [10] and was confirmed by the ^{13}C-NMR spectra of epoxides **14**, **18** (^3J(*H*–C(4), *C*–C(5)) = 4–5 Hz) and **15**, **19** (^3J(*H*–C(4), *C*–C(5)) < 1 Hz; *Scheme 2*). Compounds **18** and **19** were obtained as a 1:1.5 mixture on treatment of diene **17** [5] with 1 mol-equiv. of m-$ClC_6H_4CO_3H$ in CH_2Cl_2 (20 °C). Under the same conditions, triene **13** [11] gave a 1.3:1:1 mixture of the monoepoxides **14**/**15**/**16** (see *Exper. Part*).

All ^{1}H-NMR signals of the 360-MHz spectra of **7**–**12** could be assigned by double-irradiation experiments. The distinction between H*exo vs.* H*endo* at C(3) and C(6) in **7** and **8** was confirmed by NOE's measured for H*endo*–C(3) and H*endo*–C(6) and not for

Scheme 2



H*exo*–C(3) and H*exo*–C(6) while irradiating H*endo*–C(9) and H*endo*–C(10). The signs of the coupling constants in **11** were assigned by computer simulation. We assume the same signs for J(H,H) in **7**–**10** and **12** as the ^{1}H-NMR patterns of H–C(3), H–C(5), and H–C(6) were all very similar in **7**–**12**. They were consistent with observed geminal [12], vicinal [12][13], allylic [12–14], and homoallylic [12] coupling constants. The sign of ${}^{5}J$(H,H) between the bridgehead and allylic methylene H-atoms could not be determined. We assume it to be positive as negative ${}^{5}J$(H,H) are usually observed only when there are two different paths for the homoallylic coupling [14][15] (through bond or/and through space [16]), which is not the situation here. The homoallylic coupling constants and the δ_H of H–C(3) and H–C(6) of **7**–**12** are reported in *Table 1*. H*exo*–C(3) and H*exo*–C(6) are more deshielded than H*endo*–C(3) and H*endo*–C(6), the difference in δ_H being about the same for bicyclo[2.2.1]heptene and 7-oxabicyclo[2.2.1]heptene derivatives and independent of the nature of the substituents at C(4), C(9), and C(10).

The optimum structure of cyclohexa-1,4-diene is planar [17], although substitution can induce puckering of the ring [18]. In **7**–**12**, the vicinal ${}^{3}J$(H–C(5), H–C(6)) varied between 3.2–3.4 Hz for H*endo*–C(6) and between 3.6–3.8 Hz for H*exo*–C(6). Following *Garbisch*'s empirical correlation [19], one estimates dihedral angles of 63–67° between the H*endo*–C(6) and H–C(5) and of 56–60° between the H*exo*–C(6) and H–C(5) bonds, thus suggesting a small puckering of 3–10° of the C(3) and C(6) methylene C-atoms toward the *endo*-face. The ${}^{5}J$(H–C(3), H–C(6)) can be correlated with the cyclohexadiene conformation [17] [18a] [20]. The ratios ${}^{5}J$(H*endo*–C(3), H*endo*–C(6))/${}^{5}J$(H*endo*–C(3), H*exo*–C(6)) and ${}^{5}J$(H*endo*–C(3), H*endo*–C(6))/${}^{5}J$(H*exo*–C(3), H*endo*–C(6)) varied between 1.18 and 1.28 in **7**–**12**, whereas the ratios ${}^{5}J$(H*exo*–C(3), H*exo*–C(6))/${}^{5}J$(H*exo*–C(3), H*endo*–C(6)) and ${}^{5}J$(H*exo*–C(3), H*exo*–C(6))/${}^{5}J$(H*endo*–C(3), H*exo*–C(6)) varied between 1.02 and 1.15. This is consistent also with a small ring-puckering angle of 5–10° toward the *endo*-face of **7**–**12**.

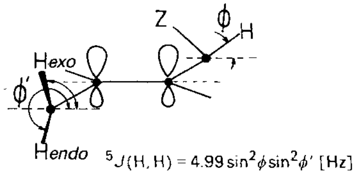
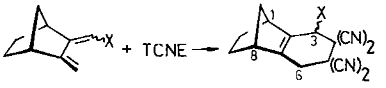


Fig. 1

Very satisfactory correlations have been obtained between experimental and calculated ${}^{5}J$(H,H) [13][21]. The geometrical dependence of π-contribution to the homoallylic coupling constant is adequately described by ${}^{5}J(\mathrm{H,H}) = 4.99 \cdot \sin^2\phi \sin^2\phi'$[13a] where ϕ and ϕ' denote the dihedral angles which are depicted in *Fig. 1*. In norbornenes, ϕ is evaluated to 17 ± 3° [22][23], in 7-oxanorbornenes to 23 ± 3° [23]. With $\phi' = 130 \pm 5°$ and $\phi' = 240 \pm 5°$ for H*exo* and H*endo*, respectively, at C(3) and C(6) one calculates ${}^{5}J$(H–C(1), H*exo*–C(6)) = ${}^{5}J$(H–C(8), H*exo*–C(3)) = 0.15–0.4 Hz and ${}^{5}J$(H–C(1), H*endo*–C(6)) = ${}^{5}J$(H–C(8), H*endo*–C(3)) = 0.2–0.5 Hz for **7** and 0.3–0.65 Hz and 0.4–0.8 Hz for **8**–**12**. This contrasts with the experimental values reported in *Table 1*. No inter-ring ${}^{5}J$(H,H) (< 0.2 Hz) could be detected for H*endo*–C(3) and H*endo*–C(6), whereas at ${}^{5}J$(H,H) = 0.8 Hz in **7** and 1.1–1.4 Hz in **8**–**12** was measured for H*exo*–C(3) and H*exo*–C(6). CNDO/2 and INDO calculations on model molecules (see below, *Table 3* and *Fig. 3*) predict larger inter-ring homoallylic coupling constants than those observed with **7**–**12**; nevertheless, the calculated ^5J(H,H) are larger for H*exo*–C(3) and H*exo*–C(6) than for the corresponding *endo*-protons, in agreement with our findings. This suggests that the σ-framework contributes significantly in differentiating the long-range coupling constants reported here.

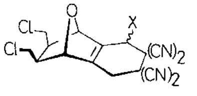
Scheme 3



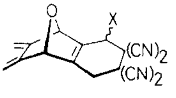
20 X = Br
21 X = MeO

22 X = *endo*-Br
23 X = *exo*-Br
24 X = *endo*-MeO
25 X = *exo*-MeO

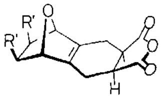
Similar observations were also made with cyclohexenes **22**–**25** annellated to bicyclo[2.2.1]hept-2-enes (obtained by tetracyanoethylene (TCNE) additions to the dienes **20** and **21**)[2]) and 7-oxabicyclo[2.2.1]heptenes **26**–**34** (*Scheme 3*) whose structure was given by combustion analysis, mode of formation, and spectral data. Adducts **26**–**30** and their 360-MHz-^{1}H-NMR characteristics have already been described in detail [5]. Irradiation of the H*endo*–C(9), H*endo*–C(10) signals led to a NOE on the H*endo*–C(3) and H*endo*–C(6) signals of **22**–**25** [5][17]. The ^4J(H,H) coupling constants between H–C(1), H–C(8) and H*exo*–C(6), H*exo*–C(3) were systematically larger (0.3–0.5 Hz) than those between H–C(1), H–C(8) and H*endo*–C(6), H*endo*–C(3) (< 0.2 Hz), respectively.



26 X = *endo*-Cl
27 X = *exo*-Cl
28 X = *endo*-MeO
31 X = H



29 X = *endo*-MeO
30 X = *exo*-MeO
32 X = H



33 R' = H
34 R' = CH_2Cl

As for **7**–**12**, the δ_H of H*exo*–C(3) and H*exo*–C(6) was slightly larger than that of the corresponding H*endo*'s ($\Delta\delta_H$ = 0.14 ppm in **22** and **24**, 0.37 ppm in **23**, 0.29 ppm in **25**, and 0.44 ppm in **30** [5] for the 2 H–C(6); see *Table 1*). Half chairs are expected for the cyclohexene-tetracarbonitriles **22**–**32** with the substituent at C(3) in a pseudoequatorial position. This was confirmed by the analysis of the intra-ring ^5J(H,H) [5][25] and by comparison with the observed and simulated ^{1}H-NMR spectra of 3-chloro-cyclohex-4-ene-1,1,2,2-tetracarbonitrile (see *Table 2*, *Fig. 2*). As for the cyclohexa-1,4-dienes **7**–**12**, the inter-ring ^5J(H,H) measured between H*exo*–C(3) and H–C(8) in **22** and **24** (0.8 ± 0.15 Hz) and **26** and **28** (1.1–1.2 Hz) as well as between H–C(1) and H*exo*–C(6) in **22**–**25** (0.8 ± 0.15 Hz) and **26**–**30** (1.1–1.4 Hz) were significantly larger than

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[2]) The synthesis of the new dienes **20** and **21** and their *Diels-Alder* stereo-selectivity will be reported elsewhere. Preliminary studies suggest an *exo*-face selectivity for the addition of TCNE, in contrast with *endo*-face selectivity usually observed for 4,7-methano-4,5,6,7-tetrahydro-2*H*-indene and derivatives [24].

Table 1. *^{1}H-NMR Spectra (360 MHz) of Cyclohexa-1,4-dienes* **7–12** *and Cyclohexenes* **22–27**. Coupling constants > 0.2 Hz. Chemical shifts [ppm, internal TMS δ_H = 0.0 ppm] for H−C(3) and H−C(6)a).

Compound	**7**b)c)	**8**b)c)	**9**c)	**10**c)	**11**c)	**12**c)	**22**d)	**23**d)	**24**d)	**25**d)	**26**e)	**27**e)
^{2}J(H*endo*−C(3), H*exo*−C(3))	−22.0	−22.2	−22.5	−22.4	−22.3	−22.5	–	–	–	–	–	–
^{2}J(H*endo*−C(6), H*exo*−C(6))	−24.0	−24.0	−23.8	−23.4	−23.7	−23.8	−18.4	−18.4	−18.4	−18.6	−18.9	−18.9
^{3}J(H−C(5), H*exo*−C(6))	3.6	3.8	3.8	3.6	3.8	3.7	–	–	–	–	–	–
^{3}J(H−C(5), H*endo*−C(6))	3.2	3.6	3.4	3.4	3.4	3.4	–	–	–	–	–	–
^{4}J(H−C(1), H*exo*−C(3))	0.3	0.3	0.4	0.4	0.4	0.3	0.3	–	0.3	–	0.4	–
^{4}J(H*endo*−C(3), H−C(5)	−2.0	−1.8	−1.8	−2.0	−1.8	−1.7	–	–	–	–	–	–
^{4}J(H*exo*−C(3), H−C(5))	−1.8	−1.6	−1.7	−1.8	−1.6	−1.5	–	–	–	–	–	–
^{4}J(H*exo*−C(6), H−C(8))	0.3	0.3	0.3	0.3	0.5	0.4	0.3	0.3	0.3	0.3	0.5	0.5
^{5}J(H−C(1), H*endo*−C(6))	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
^{5}J(H−C(1), H*exo*−C(6))	0.8	1.3	1.1	1.1	1.4	1.2	0.8	0.8	0.8	0.8	1.2	1.1
^{5}J(H*endo*−C(3), H−C(8))	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	–	< 0.2	–	< 0.2	–	< 0.2
^{5}J(H*exo*−C(3), H−C(8))	0.8	1.4	1.1	1.1	1.4	1.3	0.8	–	0.8	–	1.1	–
^{5}J(H*endo*−C(3), H*endo*−C(6))	10.2	9.8	9.5	9.8	9.4	9.8	–	1.6	–	1.6	–	1.8
^{5}J(H*endo*−C(3), H*exo*−C(6))	8.0	8.0	7.8	8.0	7.8	7.8	–	3.4	–	3.0	–	3.7
^{5}J(H*exo*−C(3), H*endo*−C(6))	8.3	8.2	8.0	8.2	7.9	8.0	3.4	–	3.0	–	3.7	–
^{5}J(H*exo*−C(3), H*exo*−C(6))	8.5	8.4	8.9	9.2	9.0	8.5	2.2	–	2.2	–	2.5	–
δ(H*endo*−C(3)	2.54	2.66	2.96	2.98	2.82	2.85	–	5.11	–	4.34	–	5.14
δ(H*exo*−C(3))	2.75	3.04	3.32	3.29	3.22	3.20	5.34	–	4.53	–	5.42	–
δ(H*endo*−C(6))	2.19	2.21	2.51	2.52	2.50	2.46	3.16	3.06	3.22	3.15	3.26	3.25
δ(H*exo*−C(6))	2.37	2.58	2.78	2.79	2.75	2.70	3.30	3.43	3.36	3.44	3.54	3.58

a) For further ^{1}H-NMR data, see *Exper. Part* and [5].

b) ^{5}J(H*exo*−C(6), H*endo*−C(9)) = 0.3 Hz in **7** and 0.5 Hz in **8**; ^{5}J(H*exo*−C(3), H*endo*−C(10)) = 0.4 Hz in **7** and **8**; ^{5}J(H*endo*−C(3), H*exo*−C(10)) = 0.4 Hz in **7** and 0.3 Hz in **8**.

c) In C_6D_6.

d) In $CDCl_3$.

e) In CD_3COCD_3.

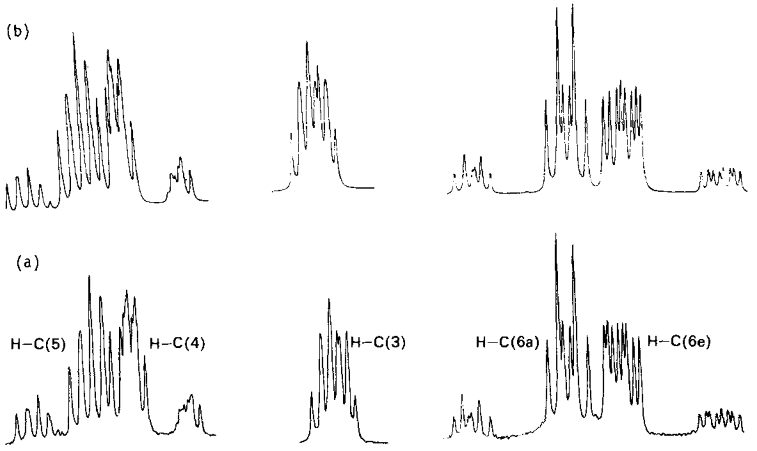
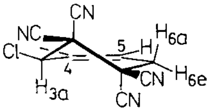


Fig. 2. *(*a*) Experimental spectrum and (*b*) simulated (LAOCOON IV) spectrum of 3-chlorocyclohex-4-ene-1,1,2,2-tetracarbonitrile.* No line fitting was required: δ_H and J(H,H) were read directly from the experimental spectrum. The simulation was made to confirm the signs of J(H,H).

Table 2. *^{1}H-NMR Spectrum (360 MHz, $CDCl_3$) of 3-Chlorocyclohex-4-ene-1,1,2,2-tetracarbonitrile*

	δ_H = 6.04 (H–C(5)); 5.99 (H–C(4)); 5.12 (H–C(3a)); 3.28 (H–C(6a)); 3.22 (H–C(6e)) ^{2}H(6a,6e) = 18.8 ± 0.2 Hz ^3J(3a,4) = 2.0; ^3J(4,5) = 10.8; ^3J(5,6a) = 2.4 ^3J(5,6e) = 5.0 ^4J(3a,5) = −2.3; ^4J(4,6a) = −2.7; ^4J(4,6e) = −1.7 ^5J(3a,6a) = 3.4; ^5J(3a,6e) = 1.7

^5J(H–C(1), H*endo*–C(6)) (< 0.2 Hz) for **22**, **24**, **26**, **28**, and **29**. With **31**–**34**, for which only partial analysis of the 360-MHz-^{1}H-NMR spectra was possible, we recorded similar inter-ring ^5J(H,H)'s: ^5J(H–C(1), H*exo*–C(6)) = ^5J(H–C(8), H*exo*–C(3)) = 0.8–1.0 Hz and ^5J(H–C(1), H*endo*–C(6)) = ^5J(H–C(8), H*endo*–C(3)) < 0.2 Hz.

Interestingly, the intra-ring ^5J(H*exo*–C(3), H*exo*–C(6)) (2.2 Hz in **22** and **24**; 2.4–2.5 Hz in **26**, **28**, and **29**) between a pseudoequatorial and a pseudoaxial proton was systematically larger than the corresponding ^5J(H*endo*–C(3), H*endo*–C(6)) (1.6 Hz in **23** and **25**; 1.8 Hz in **27**; 1.6 Hz in **30**). However, the *trans*-coupling constants ^5J(H*exo*–C(3), H*endo*–C(6)) and ^5J(H*endo*–C(3), H*exo*–C(6)), (3.4 Hz in **22**, **23**; 3.0 Hz in **24**, **25**; 3.7 Hz in **26**, **27**; 3.1 Hz in **29**, **30**) had similar values.

Discussion. – The *Barfield*'s relationship used above to evaluate the inter-ring homoallylic coupling constant ^5J(H,H) of our bicyclo[2.2.1]hept-2-ene systems considers only the π-contributions to the long-range coupling constants, and that, for unstrained model molecules. The strain of our polycyclic systems may enhance the σ-skeleton contributions and thus explain the deviations between our observed values of ^5J(H,H) and those calculated by the *Barfield*'s relationship. In order to test this hypothesis, we have carried out a number of coupling-constant calculations on the model molecules **35**–**38** using INDO and CNDO/2 wave functions [26] (see *Table 3*). The geometries used in these calculations were minimized geometries as obtained by the MNDO technique [27]. In the cases of the cyclohexa-1,4-dienes **35** and **36**, complete geometry minimization led to planar cyclohexadiene moieties annellated to planar bicyclo[2.2.1]hept-2-ene systems. With the cyclohexenes **37** and **38**, the MNDO-minimized geometries gave, as expected, half-chair conformations, also with a planar endocyclic double bond. X-ray crystallographic data [22–24] as well as *ab-initio* STO 3G MO calculations [28] suggested non-planar double bonds for the bicyclo[2.2.1]hept-2-ene systems. We thus considered the possible effect of this π-anisotropy on the inter-ring ^5J(H,H) coupling constant and repeated the INDO and CNDO/2 calculations for geometries of **35**–**38** with a non-planar double bond at C(2), C(7), in which the alkyl substituent were bent towards the *endo*-face by 15 degrees (angle α; all other geometry parameters were optimized by the MNDO technique). We completed our calculations by evaluating the inter-ring homoallylic coupling constants ^5J(H–C(1), H*exo*–C(6)) for cyclohexa-1,4-diene and cyclohexene moieties blocked in boat conformations, once bent towards the *exo*-face (**35X**–**38X**), the other time bent towards the *endo*-face (**35N**–**38N**). In the case of **37** and **38**, these two conformations corresponded to energy wells (the mirror plane of symmetry was imposed in the MNDO calculations). In order to evaluate the effect of a possible puckering of the cyclohexadiene ring in **35** and **36** (see our NMR data for **7**–**12**), we also calculated the inter-ring ^5J(H,H) coupling constants for boat conformations **35X**, **36X** and **35N**, **36N** in

Table 3. *Calculated Inter-Ring H,H Homoallylic Coupling Constants [Hz] for the Bridgehead Proton H–C(1) with H*endo- *and H*exo*–C(6) in 7-Oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene* (**35**), *Tricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene* (**36**), *7-Oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene* (**37**), *and Tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene* (**38**)

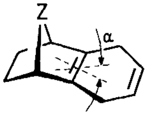
	MNDO-Minimized geometries (planar π–C(2),C(7) double bond)				
	ΔH_f°(MNDO) [kcal/mol]	^5J(H,H)	calc. by INDO	^5J(H,H)	calc. by CNDO/2
		H*endo*	H*exo*	H*endo*	H*exo*
35	1.9	0.93	2.68	0.55	1.72
36	26.1	0.49	1.69	0.18	1.03
37[a])	-26.34	0.97	2.52	0.59	1.63
38[a])	1.79	0.44	1.60	0.21	0.99
Unstable boat conformers (see text)					
35X	0.09	1.49	2.0	0.9	1.28
35N	0.00	0.42	2.85	0.20	1.81
36X	27.95	0.71	1.38	0.32	0.87
36N	27.91	0.30	1.69	0.09	0.99
37X	-24.01	1.5	2.01	0.94	1.31
37N	-24.07	0.3	2.87	0.16	1.83
38X	4.08	0.69	1.41	0.34	0.91
38N	4.07	0.25	1.55	0.08	0.94

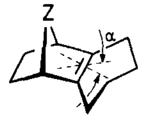
	With non-planar π–C(2),C(7) double bond, the six-membered ring bending towards the *endo*-face by $\alpha = 15°$				
	ΔH_f°(MNDO) [kcal/mol]	^5J(H,H)	calc. by INDO	^5J(H,H)	calc. by CNDO/2
		H*endo*	H*exo*	H*endo*	H*exo*
35	0.85	0.93	3.14	0.57	2.07
36	29.1	0.45	2.15	0.23	1.42
37[a])	-23.46	0.91	2.93	0.62	2.01
38[a])	4.88	0.46	2.08	0.39	1.35
Unstable boat conformers (see text)					
35X	2.57	1.75	2.60	1.14	1.71
35N	2.67	0.31	3.0	0.16	2.04
36X	30.59	0.90	1.84	0.49	1.19
36N	30.83	0.28	2.06	0.10	1.30
37X	-21.45	1.72	2.5	1.17	1.67
37N	-21.0	0.26	3.0	0.10	2.0
38X	6.79	0.92	1.89	0.55	1.24
38N	7.29	0.24	1.89	0.08	1.22

[a]) Average values ^5J(H–C(1), H–C(6)) and ^5J(H–C(8), H–C(3)) (equilibrium of half-chairs).

which the cyclohexadiene ring were bent towards the *exo*- and the *endo*-face, respectively, by an angle β of 20 degrees. Our calculations are summarized in *Table 3*.

Our semi-empirical calculations predict a larger inter-ring ^5J(H,H) value for the allylic H*exo* than H*endo* at C(3), C(6) of the tricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene and tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene systems and this *independently* of the conformation of the cyclohexa-1,4-diene and cyclohexene moieties, respectively. As expected from the angular dependence of ^5J(H,H) (see *Fig. 1*), puckering of the six-membered ring (boat conformers **35X**–**38X**) towards the *exo*-face leads to smaller ^5J(H–C(1), H*exo*–C(6))/ ^5J(H–C(1), H*endo*–C(6)) ratio than puckering towards the *endo*-face (boat conformers


Z=O: **35**
Z=CH$_2$: **36**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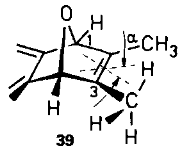
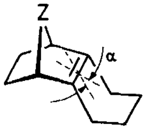
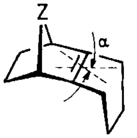
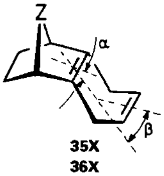
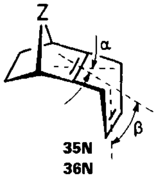

39


Z=O: **37X**
Z=CH$_2$: **38X**


37N
38N


35X
36X


35N
36N

35N–38N, see *Table 3*). The pyramidalization of the C(2),C(7) double bond with the annellated six-membered ring bending towards the *endo*-face almost always increases the calculated inter-ring homoallylic coupling constants. This increase is larger for ^5J(H–C(1),H*exo*–C(6)) than for ^5J(H–C(1),H*endo*–C(6)). The smaller values calculated for the bicyclo[2.2.1]hept-2-enes (**36, 38**) than for the 7-oxabicyclo[2.2.1]hept-2-enes (**35, 37**) are consistent with the smaller ($\phi = 17 \pm 3°$) than for the latter ($\phi = 23 \pm 3°$), in agreement with the X-ray data available [22–24] and also the *ab-initio* STO 3G calculations [28].

To further confirm the conformational dependence of the calculated inter-ring ^5J(H,H), we calculated ^5J(H–C(1),H–CH$_2$–C(3)) in 2,3-dimethyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**39**; MNDO-minimized geometries) as a function of the angle ϕ' of rotation of the CH$_3$ group at C(3). Our results are summarized in *Fig. 3* for a planar endocyclic double bond at C(2),C(3) (as obtained by the MNDO minimization) and for a structure in which the CH$_3$ groups are bent towards the *endo*-face by $\alpha = 10$ degrees [22].

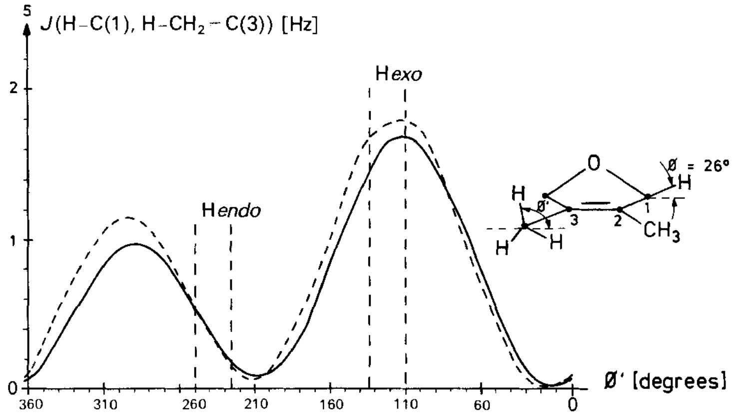


Fig. 3. *Angular (ϕ') dependance of the calculated (INDO) ^5J(H–C(1),H–CH$_2$–C(3)) in* **39**. ——: for a planar π–C(2),C(3) double bond (MNDO minimized geometry). – – –: for a non-planar π–C(2),C(3) double bond with the CH$_3$ groups bending towards the *endo*-face by $\alpha = 10°$.

It is interesting to note that the calculated ^5J(H–C(1), H–CH_2–C(3)) values are always larger for H*exo* ($\phi' = 0$–$180°$) than for H*endo* ($\phi' = 180$–$360°$) of the CH_3 group. For angle values $\phi' = 110$–$135°$, corresponding to H*exo*–C(3) in 11-oxatricyclo[6.2.1.$0^{2,7}$]undec-2(7)-enes, ^5J(H,H) is calculated to be *ca.* 4 times larger than ^5J(H,H) obtained with $\phi' = 225$–$250°$, corresponding to H*endo*–C(3).

Conclusion. – The inter-ring homoallylic coupling constants between the bridgehead protons of the bicyclo[2.2.1]hept-2-enes and 7-oxabicyclo[2.2.1]hept-2-enes and the allylic methylene protons of the annellated cyclohexa-1,4-dienes and cyclohexenes can be used to establish the relative configuration of the latter protons. Applications of this analytical tool are presented in the accompanying paper. An X-ray crystalline structure of an 7-oxabicyclo[2.2.1]hepta-2,5-diene doubly annellated with cyclohexene rings confirms its validity [29].

Acknowledgment is made to *Hoffmann-La Roche & Co. AG*, Basel, the *Fonds Herbette*, Lausanne, and the *Swiss National Science Foundation* for generous financial support. We are grateful to Prof. *J. Lauterwein* for help in the measurements of high-field ^{1}H-NMR spectra and to the referee for very pertinent and useful comments.

Experimental Part

General. See [2]. ^{1}H-NMR spectra: *Bruker WH 360 FT* spectrometer, at 303 K, *Aspect 2000* data system. All spectra were run with 32 K data points over 2500 Hz with acquisition time of 6.5–8 s and digital resolution of 0.11 Hz. Single detection and phase cycling were used. The *Bruker* microprogram was used for direct accumulation of NOE difference spectra. All solutions (0.1 to 0.2M) were degassed on the vacuum line (freeze/thaw cycles) and sealed under vacuum in 5-mm *Pyrex* tubes. Spectra simulations were performed on standard P.A.N.I.C. software on *Aspect 2000* (LAOCOON IV). No line fitting was required. The chemical shifts and apparent coupling constants were read directly from the experimental spectra. The simulations were made to confirm the sign and the values of the coupling constants. Combustion analyses were performed by Dr. *I. Beetz*, Mikroanalytisches Laboratorium, D-8640 Kronach.

Synthesis of the Cyclohexa-1,4-dienes and Cyclohexenes Annellated to Bicyclo[2.2.1]hept-2-enes. None of the procedures given below has been optimized.

Methyl Tricyclo[6.2.1.$0^{2,7}$]undeca-2(7),4-diene-4-carboxylate (**7**). See [30].

Methyl 11-Oxatricyclo[6.2.1.$0^{2,7}$]undeca-2(7),4-diene-4-carboxylate (**8**). A soln. of 2,3-dimethylidene-7-oxatrinorbornane (**4**; 0.22 g, 1 mmol; prepared according to [7]) and methyl propynoate (0.23 g, 1.3 mmol) in anh. toluene (3 ml) was stirred at 110° for 4 h. After evaporation *i.v.*, the residue was filtered on silica gel (10 g; AcOEt/petroleum ether 2:5). After evaporation, **8** was recrystallized from CCl_4 (5 ml) yielding 0.174 g (84%) of colourless crystals, m.p. 85–86°. UV (EtOH/H_2O 95:5): 219 (2500). IR (KBr): 3000, 2960, 2840, 1720, 1690. ^{1}H-NMR (C_6D_6): 6.81 (*m*, H–C(5)); 4.61 (*m*, H–C(1)); 4.54 (*m*, H–C(8)); 3.4 (*s*, CH_3O); 3.05 (*m*, H*exo*–C(3)); 2.65 (*m*, H*endo*–C(3)); 2.55 (*m*, H*endo*–C(6)); 2.21 (*m*, H*endo*–C(6)); 1.63 (*m*, H*exo*–C(9), H*exo*–C(10)); 0.83 (*m*, H*endo*–C(9), H*endo*–C(10)); attributions confirmed by NOE measurements between H*endo*–C(3), H*endo*–C(6) and H*endo*–C(9), H*endo*–C(10). MS (70 eV): 206 (5), 205 (7), 191 (10), 178 (44), 175 (16), 170 (21), 163 (21), 147 (37), 115 (100). Anal. calc. for $C_{12}H_{14}O_3$ (206.24): C 69.88, H 5.84; found: C 69.78, H 6.87.

(9,10-Dimethylidene-11-oxatricyclo[6.2.1.$0^{2,7}$]undeca-2(7),4-dien-4-yl) Methyl Ketone (**9**). A soln. of 2,3,5,6-tetramethylidene-7-oxatrinorbornane [8] (**5**; 0.15 g, 1.03 mmol) and 3-butyn-2-one (0.2 g, 2.4 mmol) in anh. toluene (1 ml) was stirred at 90° for 5 h. The mixture was filtered on silica gel (8 g, AcOEt/petroleum ether 1:1) and crystallized from AcOEt yielding 0.217 g (93%) of **9** as colourless crystals, m.p. 101–102°. UV (EtOH/H_2O 95:5): 235 (3400). IR (KBr): 2990, 2890, 2880, 2820, 1780, 1670, 1630, 1430, 1390, 1370, 1280, 1270, 1210, 1150, 1090, 970, 890, 840, 800, 760. ^{1}H-NMR ($CDCl_3$): 6.26 (*m*, H–C(5)); 5.29, 5.26, 5.01, 4.96 (4 br. *s*, CH_2=C(9), CH_2=C(10)); 4.95, 4.94 (2*m*, H–C(1), H–C(8)); 3.32 (*m*, H*exo*–C(3)); 2.96 (*m*, H*endo*–C(3)); 2.78 (*m*, H*exo*–C(6)); 2.51 (*m*, H*endo*–C(6)). MS (70 eV): 214 (13), 199 (6), 185 (56), 171 (38), 162 (22), 161 (18), 144 (69), 141 (53), 128 (100), 91 (24), 85 (18), 77 (20), 65 (29). MS (HR): 214.09729 ($\Delta M/M = 9$ ppm; $C_{14}H_{14}O_2$, calc. 214.09934).

Methyl 9,10-Dimethylidene-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate (**10**). Same procedure as for the preparation of **9**, but using methyl propynoate (0.252 g, 2.98 mmol) instead of butynone. Yield: 0.214 g (91%), colourless crystals, m.p. 115–116°. UV (EtOH/H_2O 95:5): 226 (5800). IR (KBr): 3000, 2960, 2900, 1720, 1640, 1430, 1330, 1250, 1110, 1050, 970, 950, 890, 850. ^{1}H-NMR (C_6D_6): 7.0 (*m*, H–C(5)); 5.3, 5.1 (2 br. *s*, CH_2=C(9), CH_2=C(10)); 5.0 (*m*, H–C(1), H–C(8)); 3.8 (*s*, CH_3O); 3.0 (br. *m*, 2 H–C(3), 2 H–C(6)). MS (70 eV): 230 (3), 229 (11), 215 (18), 199 (34), 187 (31), 171 (13), 115 (100). Anal. calc. for $C_{14}H_{14}O_3$ (230.26): C 73.03, H 6.13; found: C 72.96, H 6.30.

*[10-*exo*-10-*endo*-(Epoxymethano)-9-methylidene-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-dien-4-yl] Methyl Ketone* (**11**). A soln. of the monoepoxide **6** of 2,3,5,6-tetramethylidene-7-oxatrinorbornane [9] (0.16 g, 0.99 mmol) and 3-butyn-2-one (0.2 g, 2.4 mmol) in anh. toluene was stirred at 110° for 8 h. Filtration on silica gel (10 g, AcOEt/petroleum ether 1:1) and solvent removal *i.v.* gave **11** and its regioisomer *[9-*exo*,9-*endo*-(epoxymethano)-10-methylidene-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-dien-4-yl methyl ketone* as minor product. The mixture was chromatographed on silica gel (16 g, AcOEt/petroleum ether 3:7). The first fraction contained **11** which was recrystallized from pentane/Et_2O: 0.105 g (46%), colourless needles, m.p. 153–154°. UV (EtOH/H_2O 95:5): 226 (3600), 254 (sh, 1400). IR (KBr): 3000, 2840, 2810, 1665, 1630, 1390, 1370, 1350, 1230, 1090, 970, 930, 900, 830, 810.

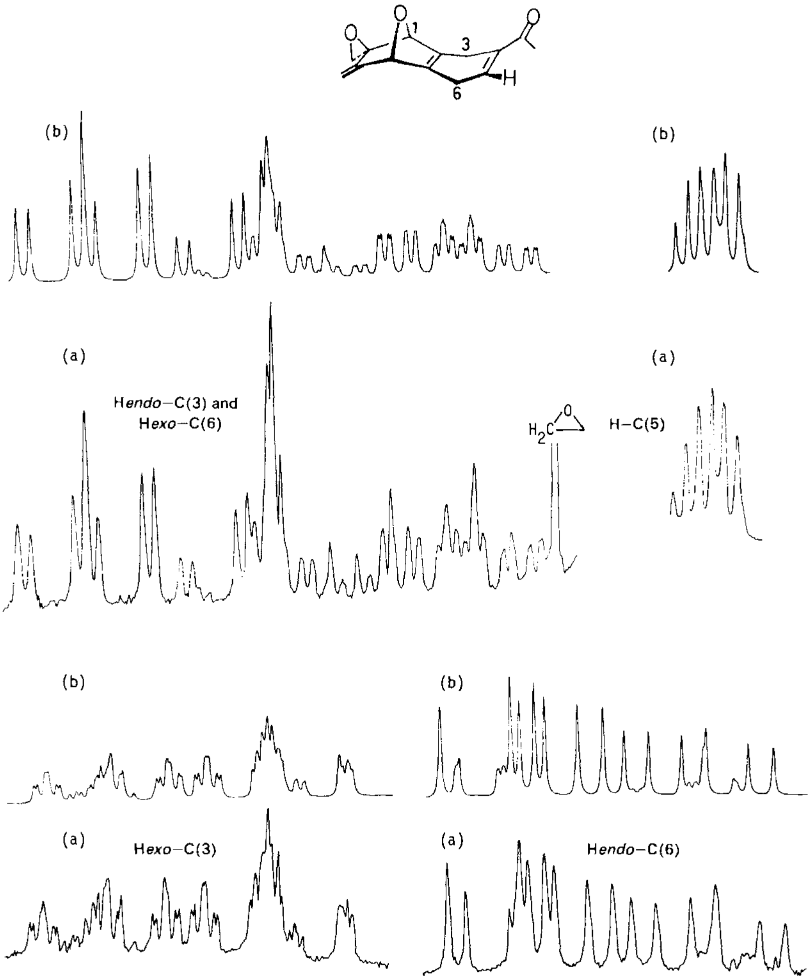


Fig. 4. *Partial experimental* (a) *and stimulated* (b) *^{1}H-NMR spectra of the cyclohexa-1,4-diene* **11** (in C_6D_6, 360 MHz)

^{1}H-NMR ($CDCl_3$): 6.8 (*m*, H–C(6)); 5.05, 4.70 (2 br. *s*, CH_2=C(9)); 4.95 (*m*, H–C(8)); 4.4 (*m*, H–C(1)); 3.5–2.5 (*m*, 2 H–C(3), 2 H–C(6)); 3.02 (2*d*, J_{gem} = 4, CH_2–C(10)); 2.3 (*s*, CH_3CO); attributions confirmed by double-irradiation experiments and LAOCOON IV simulations, see *Fig. 4*. MS (70 eV): 230 (3), 229 (8), 201 (35), 187 (86), 173 (18), 169 (51), 147 (75), 128 (38), 115 (100), 91 (60), 77 (44). Anal. calc. for $C_{14}H_{14}O_2$ (230.26): C 73.03, H 6.13; found: C 73.06, H 5.93.

The minor adduct was crystallized from the second fraction of the above chromatography: 0.062 g (27%), colourless cubic crystals, m.p. 133–134°. UV ($EtOH/H_2O$ 95:5): 227 (3600), 254 (sh, 1200). IR (KBr): 3000, 2970, 2880, 2810, 1665, 1630, 1370, 1350, 1320, 1230, 1150, 990, 970, 940, 840, 805. ^{1}H-NMR (C_6D_6): 6.7 (*m*, H–C(5)); 5.05, 4.60 (2 br. *s*, CH_2=C(10)); 4.9 (*m*, H–C(1)); 4.4 (*m*, H–C(8)); 3.3–2.6 (*m*, CH_2(3), CH_2(6)); 3.0 (2*d*, J_{gem} = 4, CH_2–C(9)); 2.3 (*s*, CH_3CO). MS (70 eV): 230 (11), 229 (7), 201 (20), 187 (80), 173 (18), 169 (50), 145 (85), 128 (69), 115 (100), 91 (70), 77 (30). Anal. calc. for $C_{14}H_{14}O_2$ (230.26): C 73.03, H 6.13; found: C 72.70, H 6.26.

*Methyl 10-*exo*,10-*endo*-(Epoxymethano)-9-methylidene-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),4-diene-4-carboxylate* (**12**). A soln. of the monoepoxide **6** (0.16 g, 0.99 mmol) and methyl propynoate (0.25 g, 2.98 mmol) in anh. toluene was stirred at 110° for 8 h. After filtration on silica gel (10 g, AcOEt/petroleum ether 1:1) and evaporation *i.v.*, the crude **12** (contaminated by 10–20% of its regioisomer) [8] was purified by 3 recrystallizations from AcOEt/hexane 3:1 (12, 8, and 4 ml) yielding 0.087 g (36%) of colourless crystals, m.p. 128–129° (the mother liquor contained the regioisomer of **12**; it could not be isolated in a pure form). UV ($EtOH/H_2O$ 95:5): 222 (3200), 253 (sh, 1800). IR (KBr): 3000, 2960, 2870, 1700, 1680, 1630, 1430, 1330, 1270, 1250, 1110, 1050, 970, 930, 840, 750, 730. ^{1}H-NMR (C_6D_6): 6.95 (*m*, H–C(5)); 5.1, 4.9 (2 br. *s*, CH_2=C(9)); 5.0 (*m*, H–C(8)); 4.4 (*m*, H–C(1)); 3.8 (*s*, CH_3O); 3.2–2.8 (*m*, CH_2(3), CH_2(6)); 3.05 (*d*, J_{gem} = 4, CH_2–C(10)). MS (70 eV): 246 (3), 243 (3), 231 (14), 215 (25), 203 (56), 187 (39), 171 (15), 135 (45), 115 (100). Anal. calc. for $C_{14}H_{14}O_4$ (264.26): C 68.28, H 5.73; found: C 68.23, H 5.84.

*5-*endo*-5-*exo*-(Epoxymethano)-6-methylidene-7-oxabicyclo[2.2.1]hept-2-ene* (**14**). A mixture of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene [11] (**13**; 1.4 g, 10 mmol), *m*-chloroperbenzoic acid (1.9 g, 10 mmol), and CH_2Cl_2 (14 ml) was stirred at 20° for 2 h. The precipitate was filtered off and washed with CH_2Cl_2 (10 ml). The org. solns. were united and washed with sat. aq. Na_2CO_3 soln. (30 ml, 3×), then with H_2O (30 ml). After drying ($MgSO_4$), *N*-phenyltriazolinedione (0.7 g) was added portionwise, until persistance of the red colour (elimination of unreacted **13** and epoxydiene **16**). After stirring at 0° for 15 h, the precipitate was filtered off and washed with CH_2Cl_2 (10 ml). After evaporation, the residue was purified by column chromatography on silica gel (70–230 mesh, AcOEt/petroleum ether 2:7) giving 2 fractions. The first fraction contained 180 mg (15%) of pure **14**, colourless liquid, b.p. 40°/0.1 Torr, miscible with all usual solvents. IR (CCl_4): 3030, 2940, 1760, 1670, 1480, 1430, 1390, 1300, 1000, 950, 850. ^{1}H-NMR ($CDCl_3$): 6.5 (*dd*, ^3J(H–C(1),H–C(2)) = 2, ^3J(H–C(2),H–C(3)) = 5.5, H–C(2)); 6.4 (*dd*, ^3J(H–C(3),H–C(4)) = 2, ^3J(H–C(3),H–C(2)) = 5.5, H–C(3)); 5.1 (br. *s*, H–C(4)); 4.95, 4.65 (2*s*, CH_2=C(6)); 3.1, 3.0 (2*d*, ^2J = 4.5, CH_2–C(5)). ^{13}C-NMR ($CDCl_3$): 143.8 (br. *s*, C(6)); 137.3 (*d*, ^1J(C,H) = 178, C(2)); 134.5 (*d*, ^1J(C,H) = 186, C(3)); 103.5 (*t*, ^1J(C,H) = 158, *C*H_2=C(6)); 83.2 (*d*, ^1J(C,H) = 174, C(1)); 79.2 (*d*, ^1J(C,H) = 160, H–C(4)); 62.3 (br. *s*, C(5)); 52.7 (*td*, ^1J(C,H) = 175, ^3J(C,H) = 5, CH_2*exo*–C(5)). MS (70 eV): 136 (3, M^+), 135 (31), 108 (39), 107 (47), 79 (81), 77 (100), 68 (47), 51 (68). Anal. calc. for $C_8H_8O_2$ (136.15): C 70.59, H 5.88; found: C 70.65, H 5.90.

*5-*exo*,5-*endo*-(Epoxymethano)-6-methylidene-7-oxabicyclo[2.2.1]hept-2-ene* (**15**). The second fraction of the above chromatography contained 140 mg (11%) of pure **15**, colourless liquid, b.p. 60°/0.1 Torr. IR (CCl_4): 3030, 2940, 2250, 1720, 1390, 1370, 1300, 1280, 1000, 900. ^{1}H-NMR ($CDCl_3$): 6.5 (*dd*, ^3J(H–C(1),H–C(2)) = 2, ^3J(H–C(2),H–C(3)) = 5.5, H–C(2)); 6.3 (*dd*, ^3J(H–C(3),H–C(4)) = 2, ^3J(H–C(2),H–C(3)) = 5.5, H–C(3)); 5.1 (br. *s*, H–C(1)); 5.0, 4.7 (2*s*, CH_2=C(6)); 4.3 (br. *s*, H–C(4)); 2.9 (br. *s*, CH_2–C(5)). ^{13}C-NMR ($CDCl_3$): 142.7 (br. *s*, C(6)); 138.6 (*d*, ^1J(C,H) = 176, C(2)); 134.6 (*d*, ^1J(C,H) = 183, C(3)); 104.2 (*t*, ^1J(C,H) = 159, CH_2=C(6)); 82.7 (*d*, ^1J(C,H) = 168) and 82.0 (*d*, ^1J(C,H) = 173, H–C(1), H–C(4)); 63.37 (br. *s*, C(5)); 49.1 (*t*, ^1J(C,H) = 174, ^3J(C,H) < 1, CH_2 *endo*–C(5)). MS (70 eV): 136 (3, M^+), 135 (19), 108 (27), 107 (40), 79 (92), 77 (100), 68 (49), 51 (67). Anal. calc. for $C_8H_8O_2$ (136.15): C 70.59, H 5.88; found: C 70.50, H 6.08.

*3-*exo*-Bromotricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**23**). A soln. of 2-(bromomethylidene)-3-methylidenetrinorbornane (**20**); 0.2 g, 1.01 mmol; obtained by Br_2 addition to 2,3-dimethylidene trinorbornane [6] (**3**) and treatment with *t*-BuOK in THF and ethylenetetracarbonitrile (TCNE; 0.13 g, 1.02 mmol) in anh. benzene (2 ml) was stirred at r.t. for 20 min. After evaporation *i.v.*, the mixture was taken up with acetone (1 ml) and purified by column chromatography on silica gel (18 g, AcOEt/petroleum ether 2:7) yielding 0.3 g of **22**/**23**. Three recrystallizations from $CHCl_3$/hexane 8:2 (7, 3, and 2 ml) yielded 0.038 g (12%) of pure **23**, colourless crystals, m.p. 183–184°. IR (KBr): 3020, 3000, 2980, 2960, 2880, 2250, 1650, 1450, 1430, 1290, 1280, 1190, 1120, 950, 710, 690. ^{1}H-NMR ($CDCl_3$): 5.11 (*m*, H–C(3)); 3.43 (*m*, H*exo*–C(6)); 3.10 (*m*, H–C(1)); 3.06 (*m*, H*endo*–C(6)); 3.0 (*m*, H–C(8)); 1.98 (*m*, H*exo*–C(9), H*exo*–C(10)); 1.62, 1.31 (*m*, CH_2(11)); 1.17 (*m*, H*endo*–C(10)); 1.12 (*m*, H*endo*–C(9)); attributions confirmed by NOE measurements. MS (70 eV): 328 (4), 326 (4), 300 (9), 298 (9), 247 (37), 220 (100), 193 (12), 142 (5), 91 (6). Anal. calc. for $C_{15}H_{11}BrN_4$ (327.18): C 55.06, H 3.38, N 17.12; found: C 55.09, H 33.30, N 17.19.

*3-*endo*-Methoxytricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**24**). A soln. of 2-(methoxymethylidene)-3-methylene trinorbornane (**21**[2]; 0.15 g, 1 mmol) and TCNE (0.13 g, 1.02 mmol) in anh. benzene (2 ml) was stirred at 20° for 10 min. After evaporation *i.v.*, the residue was dissolved in acetone (1 ml) and purified by column chromatography on silica gel (20 g, AcOEt/petroleum ether 2:7) yielding 0.25 g (86%) of **24/25**. Three recrystallizations from $CHCl_3$/hexane 3:2 (7, 5, and 1.5 ml) yielded 0.022 g (12%) of pure **24**, colourless needles, m.p. 110–111°. IR (KBr): 3010, 2980, 2960, 2260, 1450, 1440, 1370, 1330, 1290, 1250, 1100, 870, 730. ^{1}H-NMR ($CDCl_3$): 4.42 (*m*, H–C(3)); 3.83 (*s*, CH_3O); 3.36 (*dm*, H*exo*–C(6)); 3.22 (*d*, H*endo*–C(6)); 3.19 (*m*, H–C(1)); 3.03 (*m*, H–C(8)); 2.16 (*m*, H*exo*–C(9), H*exo*–C(10)); 1.78, 1.71 (2*m*, CH_2(11)); 1.66, 1.61 (2*m*, H*endo*–C(9), H*endo*–C(10)); attributions confirmed by NOE measurements. MS (70 eV): 278 (3), 251 (4), 150 (80), 122 (100), 121 (75). Anal. calc. for $C_{16}H_{14}N_4O$ (278.32): C 69.05, H 5.07, N 20.13; found: C 68.91, H 5.21, N 20.20.

The synthesis and characteristics of **22** and **25** will be described elsewhere. For the syntheses of **26**–**32**: see [5].

*11-Oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4-*exo*,5-*exo*-dicarboxylic Anhydride* (**33**). A soln. of 2,3-dimethylidene-7-oxatrinorbornane [7] (**4**; 0.13 g, 1.06 mmol) and maleic anhydride (0.125 g, 1.28 mmol) in anh. toluene was heated to 105° for 3 h. The precipitate was collected by filtration and washed with cold toluene (2 ml). Recrystallization from AcOEt (4.5 ml) yielded 0.19 g (83%) of pure **33**, colourless crystals, m.p. 187–188° (the mother liquor showed the presence of *ca.* 10% of the 4-*endo*,5-*endo* isomer). IR (KBr): 3040, 3000, 2960, 2930, 1870, 1790, 1450, 1440, 1320, 1240, 1230, 1205, 1070, 980, 920, 680. ^{1}H-NMR ($CDCl_3$): 4.88 (*m*, H–C(1), H–C(8)); 3.38 (*m*, H–C(4), H–C(5)); 2.81 (*dm*, J_{gem} = 18, H*exo*–C(3), H*exo*–C(6)); 2.41 (*dm*, J_{gem} = 18, H*endo*–C(3), H*endo*–C(6)); 1.83 (*m*, H*exo*–C(9), H*exo*–C(10)); 1.14 (*m*, H*endo*–C(9), H*endo*–C(10)). MS (70 eV): 220 (4), 193 (6), 192 (56), 164 (65), 147 (5), 120 (21), 119 (100), 118 (9), 117 (7), 92 (12), 91 (52). Anal. calc. for $C_{12}H_{12}O_4$ (220.224): C 65.44, H 5.49; found: C 65.32, H 5.49.

*9-*exo*,10-*exo*-Bis(chloromethyl)-11-oxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4-*exo*,5-*exo*-dicarboxylic Anhydride* (**34**). Same procedure as for the preparation of **33** starting with 2-*exo*,3-*exo*-bis(chloromethyl)-5,6-dimethylidene-7-oxatrinorbornane [5]: 0.19 g (83%), colourless crystals, m.p. 186–187° (the mother liquor contained *ca.* 10% of the 4-*endo*,5-*endo*-isomer). IR (KBr): 3040, 3000, 2960, 2850, 1870, 1790, 1450, 1350, 1320, 1280, 1230, 1220, 1185, 1065, 970, 920. ^{1}H-NMR ($CDCl_3$): 4.8 (*m*, H–C(1), H–C(8)); 3.7, 3.5 (2*m*, 2 CH_2Cl); 3.4 (*m*, H–C(4), H–C(5)); 2.9 (*m*, H*exo*–C(3), H*exo*–C(6)); 2.5 (*m*, H*endo*–C(3), H*endo*–C(6)); 2.1 (*m*, H–C(9), H–C(10)). MS (70 eV): 283 (0.3), 281 (1), 245 (6), 192 (35), 164 (100), 119 (86), 91 (53). Anal. calc. for $C_{14}H_{14}Cl_2O_4$ (317.168): C 53.01, H 4.45; found: C 52.85, H 4.48.

3-Chlorocyclohex-4-ene-1,1,2,2-tetracarbonitrile. TCNE (0.13 g, 1 mmol) was dissolved in 1-chlorobutadiene (5 ml, 56.5 mmol) and heated under reflux. After 8 h at 80°, the chlorobutadiene in excess was removed by distillation *i.v.* The residue was dissolved in acetone (1 ml) and purified by column chromatography on silica gel (15 g, AcOEt/petroleum ether 2:7) and recrystallization from $CHCl_3$/hexane 3:2 (9 ml): 0.174 g (80%), colourless crystals, m.p. 151–152°. IR (KBr): 3100, 3080, 2260, 1660, 1440, 1260, 1240, 1210, 875, 800, 790, 650. ^{1}H-NMR: *Fig. 2, Table 2.* MS (70 eV): 218 (1), 216 (3), 181 (10), 154 (23), 140 (13), 138 (40), 103 (8), 91 (33), 89 (100). Anal. calc. for $C_{10}H_5ClN_4$ (216.63): C 55.44, H 2.33; found: C 55.68, H 2.49.

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