

204. Synthesis and Electron-Diffraction Structure of all-*cis*-[5.5.5.5]Fenestrane

by Jan Brunvoll^{a)}, Régine Guidetti-Grept^{b)}, Istvan Hargittai^{c)}, and Reinhart Keese^{*b)}

^{a)} Physical Chemistry Division, University of Trondheim, N-7034 Trondheim

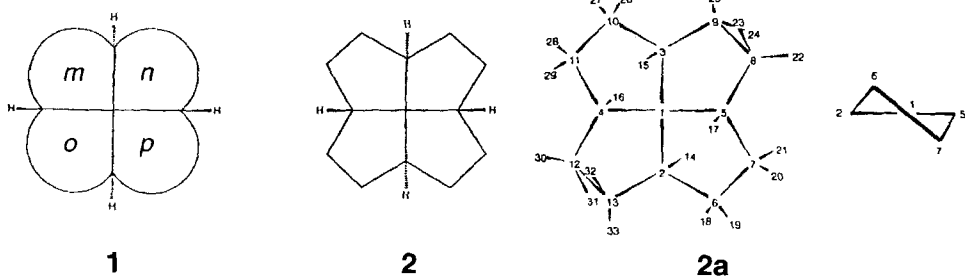
^{b)} Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern

^{c)} Institute of General and Analytical Chemistry, Budapest, Technical University and Structural Research Group of the Hungarian Academy of Sciences, H-1521 Budapest

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The efficient synthesis of all-*cis*-[5.5.5.5]fenestrane (**2**) from the readily available intermediate **3** allowed the electron-diffraction analysis of **2**. This structure analysis revealed long C–C bonds in the central C(C)₄ fragment and a twist-envelope conformation for the four cyclopentane substructures. The four bridgehead H-atoms are in a synclinal rather than an eclipsic position with an approximate *D*₂ symmetry of **2**. Planarizing distortions are evident from the opposite bond angles at the central C-atom being $116.2 \pm 0.5^\circ$ with the remaining four being $103.7 \pm 0.2^\circ$.

Introduction. – The ‘terra incognita’ of the deformation space of the tetracoordinate C-atom has long been the area where structures have two opposite bond angles larger than those of a regular tetrahedron. A unique class of hydrocarbons with this specific structural feature are the [*m.n.o.p*]fenestrans of general type **1**. Within the last two decades, considerable efforts were undertaken to prepare such compounds and to elucidate – by X-ray structure analysis – their structure [1] [2]. Computational results accompanied these explorations and led to valuable information about structure and strain of this intriguing hydrocarbons.

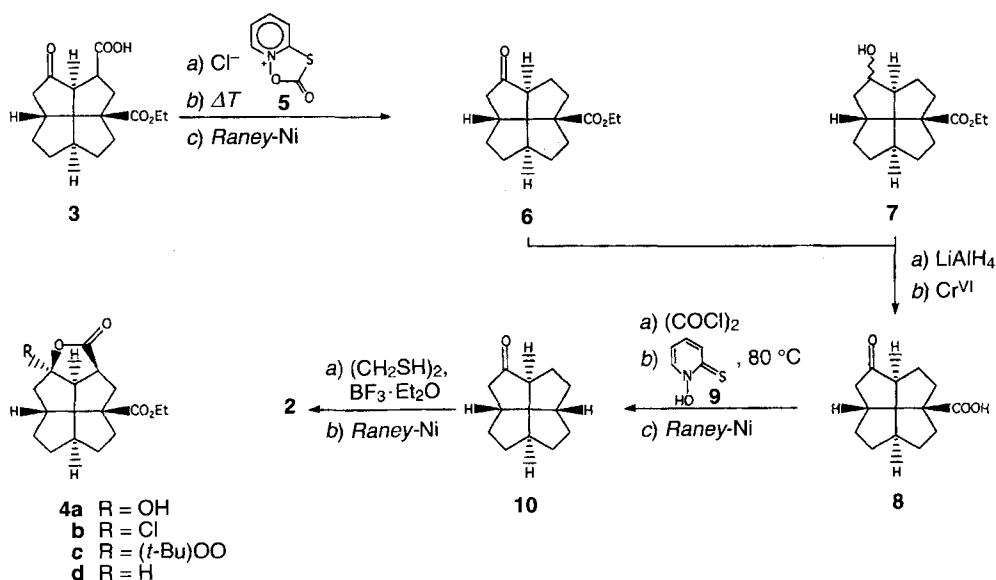


This class of tetracyclic compounds may be viewed as a circular arrangement of four small rings which share a common C-atom. Stereochemical considerations revealed that stereoisomers should exist which can be classified by their symmetry properties and should have unique structures and energy contents. Due to the lack of efficient syntheses providing larger amounts of fenestrans, only a few features of their structure and chemical properties were elucidated [3–5]. With the recent development of transition-metal induced ring-closure reactions, sufficient amounts of fenestrans became available

which is an absolute prerequisite for a thorough investigation of their structural and chemical properties. We report here an efficient synthesis of the all-*cis*-[5.5.5.5]fenestrane (**2**) and its gas-phase electron-diffraction structure analysis.

Synthesis of all-*cis*-[5.5.5.5]Fenestrane (2). – The substituted [5.5.5.5]fenestrane **3** which can be prepared from readily available precursors [6] was used for the synthesis of the unsubstituted hydrocarbon **2**. The observation that the sterically hindered COOEt group could not be saponified and that the COOH group has a strong tendency for addition to the adjacent C=O group to give **4a** led to a procedure by which the three functionalities were removed in a stepwise manner (*Scheme*). The first attempt to remove the COOH group of **3** by thermolysis of the corresponding *tert*-butyl ester was unsuccessful. Treatment of **3** with SOCl₂ led predominantly to **4b**, and the reaction of **3** with *tert*-butyl hydroperoxide and dicyclohexylcarbodiimide (DCC) gave predominantly **4c** which did not decarboxylate. Eventually, it was found that freshly prepared **3**, when treated with *Barton's* reagent **5** [7], decarboxylated readily at elevated temperature to give, after reaction with *Raney-Ni*, a mixture of **6** and **7** and a minor amount of **4d** (*Scheme*). Subsequent reduction-oxidation of **6/7** led to the keto acid **8** which could be

Scheme



transformed into ketone **10** by treatment of the corresponding acyl chloride with **9**. The all-*cis*-Fenestrane (**2**) was eventually obtained from the thioketal prepared from **10**, by treatment with *Raney-Ni*. Fenestrane **2** is a colourless hydrocarbon which solidifies between 0–5° and has a pleasant odour.

Electron-Diffraction Structure Analysis. – *Data Collection.* The electron-diffraction pattern was recorded at two camera ranges and 60-kV nominal accelerating voltage in a modified *EG-100A* apparatus [8]. A so-called membrane nozzle system [9] was used. The electron wavelength was calibrated with a TICl polycrystal sample [10].

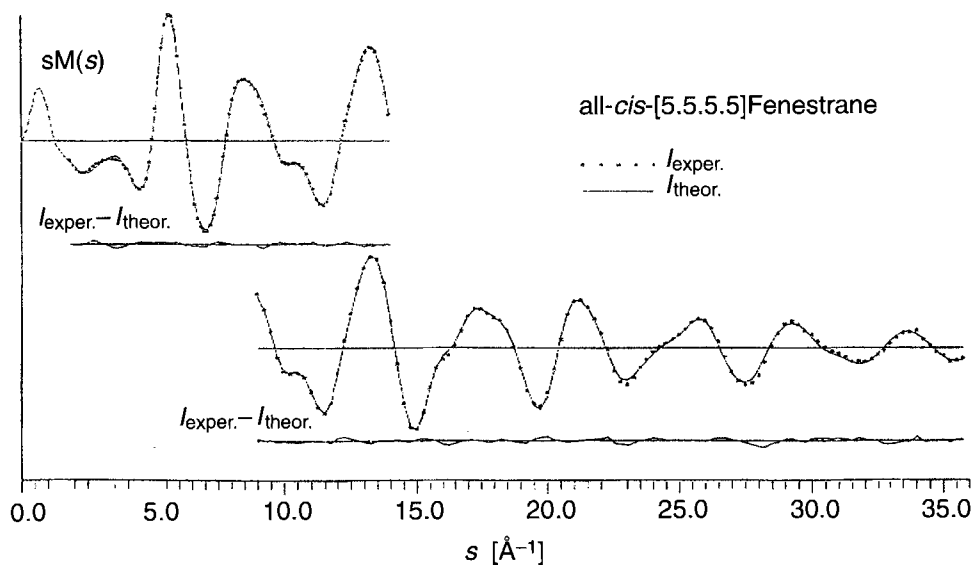


Fig. 1. Experimental ($I_{\text{exper.}}$) and theoretical ($I_{\text{theor.}}$) molecular intensities of all-*cis*-[5.5.5.5]fenestrane (**2**)

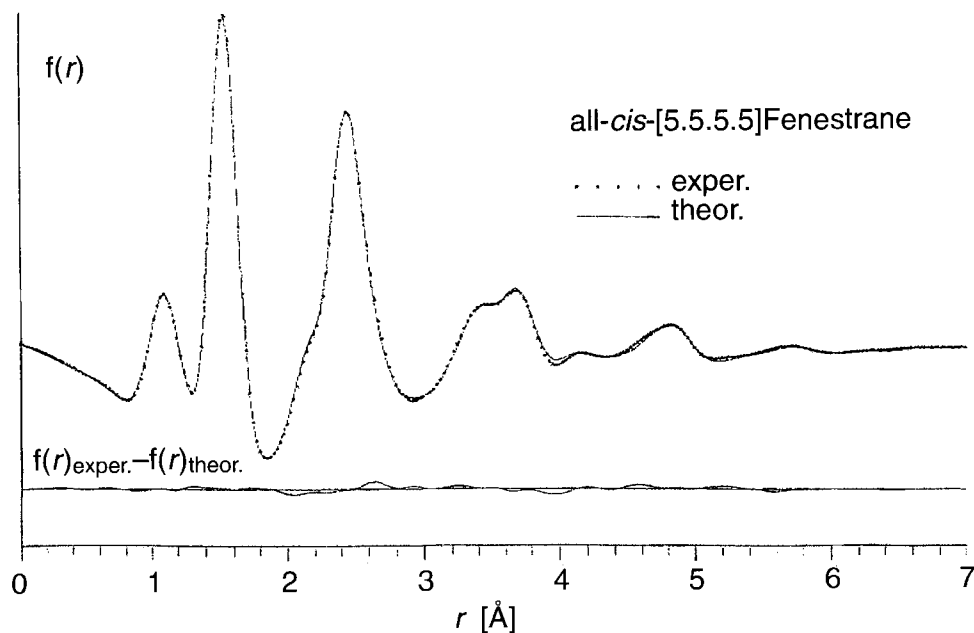


Fig. 2. Experimental ($f(r)_{\text{exper.}}$) and theoretical ($f(r)_{\text{theor.}}$) radial distributions of all-*cis*-[5.5.5.5]fenestrane (**2**). Under the assumptions of the molecular model described in the text, there are 129 different distances. The C/C contributions occur as follows: C–C bonds under the maximum at *ca.* 1.55 Å, nonbonded C·C (through 1 C-atom) at *ca.* 2.4 Å, C··C (through 2 C-atoms) under the double peak of 3.4 and 3.6 Å, and C···C at 4.1 and 4.8 Å. The most conspicuous C/H contributions are seen at 1.1 Å from the C–H bonds, at the shoulder at 2.2 Å from the C·H nonbonded distances (through 1 C-atom), and at 5.7 Å from C···H nonbonded distances (through 4 C-atoms).

Table 1. *Electron-Diffraction Structure Analysis of Fenestrane 2: Experimental Conditions*

No. of plates analyzed	Camera distance [mm]	Nozzle temp. [°C]	Wavelength [Å]	Data intervals [Å ⁻¹]	Data steps [Å ⁻¹]
5	500.4	76	0.04930	1.875–14.000	0.125
7	191.4	76	0.04930	9.00–35.75	0.25

The main experimental conditions are collected in *Table 1*. Our usual procedure of data reduction was applied [11] [12] with an empirical blackness correction for the *Kodak* electron-image plates. The total experimental intensities and final backgrounds are available as supplementary material. The molecular intensities and radial distributions are shown in *Figs. 1* and *2*. The first maximum at 1.1 Å on the radial distribution curve can be identified with the contributions of the C–H bonds, while the second maximum at *ca.* 1.55 Å with those of the C–C bonds. The rest of the radial distribution originates from contributions of nonbonded interactions.

Structure Analysis. The electron-diffraction analysis provided unequivocal evidence, independent from the NMR results and the stereochemical outcome of the synthesis, for an all-*cis*-structure **2a** of the [5.5.5.5]fenestrane¹⁾. When a plane of symmetry through C(2)–C(1)–C(3) was used as model (arbitrary numbering, see **2a**), the experimental and theoretical distributions showed considerable differences. For further optimization of the structure, the following assumptions were used: *i*) all four five-membered rings have the same bond lengths and bond angles, *ii*) mean values are taken for the pairs of bond angles C(6)–C(2)–H(14) and C(13)–C(2)–H(14), C(2)–C(6)–H(18) and C(7)–C(6)–H(18), and C(2)–C(6)–H(19) and C(7)–C(6)–H(19) as well as for all C–H bond lengths.

Allowing non-planarity for the five-membered rings, the C(6) atom may be above or below the plane through C(2)–C(1)–C(5). Considerable improvement was achieved with C(6) above the C(2)–C(1)–C(5) plane and C(12) above the C(4)–C(1)–C(2) plane at the same time. This model led to the definite improvement in the agreement between the experimental and theoretical distributions.

Table 2. *Results of the Least-Squares Refinements^{a)}*. Arbitrary numbering, see **2a**

Independent parameters	Multiplicity	r_a [Å] / < (deg)	l [Å]	
			ED ^{b)}	SP
$\Delta 1,2$	–	0.0190 (73) ^{c)}	–	–
$\Delta 6,7$	–	0.0030 (146) ^{c)}	–	–
C–H	20	1.1113 (13)	0.0800 (13)	0.0770
C(2)–C(6)	8	1.5375 (54)	0.0549 (6) ^{d)}	0.0492
C(2)–C(1)–C(3)	–	116.17 (36)	–	–
C(1)–C(2)–C(6)	–	105.37 (25)	–	–
C(6)–C(2)–H(14)	–	110.82 (131)	–	–
C(2)–C(6)–H(18)	–	108.94 (67)	–	–
C(2)–C(6)–H(19)	–	110.20 (74)	–	–

¹⁾ According to IUPAC nomenclature, all-*cis*-[5.5.5.5]fenestrane (**2**) is *cis-transoid-cis-transoid-cis-transoid-cis-transoid*-tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane and *c(is)*, *t(rans)*, *c(is)*, *t(rans)*-[5.5.5.5]fenestrane is *cis-cisoid-cis-transoid-cis-cisoid-cis-transoid*-tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane. According to *Chem. Abstr.*, [5.5.5.5]-fenestrane is dodecahydropentaleno[1,6-*cd*]pentalene.

Table 2 (cont.)

Dependent distances and angles				
C(6)–C(7)	4	1.5405 (93)	0.0550 ^{d)}	0.0493
C(1)–C(2)	4	1.5565 (27)	0.0543 ^{d)}	0.0486
C(2)·C(7)	8	2.4203 (17)	0.0736 (10) ^{e)}	0.0740
C(1)·C(6)	8	2.4607 (19)	0.0681 ^{e)}	0.0688
C(2)·C(4)	4	2.4898 (45)	0.0653 ^{e)}	0.0657
C(6)·C(13)	4	2.621 (89)	0.111 ^{e)}	0.112
C(2)·C(3)	2	2.6424 (76)	0.0779 ^{e)}	0.0783
C(6)··C(12)	4	3.2349 (50)	0.154 (4) ^{f)}	0.149
C(2)··C(11)	4	3.4408 (20)	0.110 ^{f)}	0.105
C(2)··C(9)	4	3.5044 (43)	0.118 ^{f)}	0.112
C(2)··C(8)	4	3.6617 (17)	0.0684 (29) ^{g)}	0.0801
C(2)··C(10)	4	3.7215 (39)	0.0740 ^{g)}	0.0857
C(6)··C(8)	4	3.7932 (16)	0.0825 ^{g)}	0.0942
C(6)··C(9)	4	4.0886 (61)	0.0951 (73) ^{h)}	0.133
C(6)··C(11)	2	4.6958 (54)	0.092 (57) ⁱ⁾	0.102
C(8)··C(12)	2	4.7168 (52)	0.103 ⁱ⁾	0.113
C(8)··C(13)	2	4.8805 (38)	0.0732 ^{g)}	0.0826
C(6)··C(10)	2	4.9007 (38)	0.0748 ⁱ⁾	0.0842
C(2)–C(1)–C(5)	–	106.23 (17)	–	–
C(2)–C(6)–C(7)	–	103.69 (14)	–	–
C(1)–C(2)–H(14)	–	106.71 (298)	–	–

a) Concerning the parenthesized standard deviations, see text.

b) Amplitudes refined in the groups ^{d)}, ^{e)}, ^{f)}, ^{g)}, ^{h)}, and ⁱ⁾ with assumed differences from spectroscopic calculations.

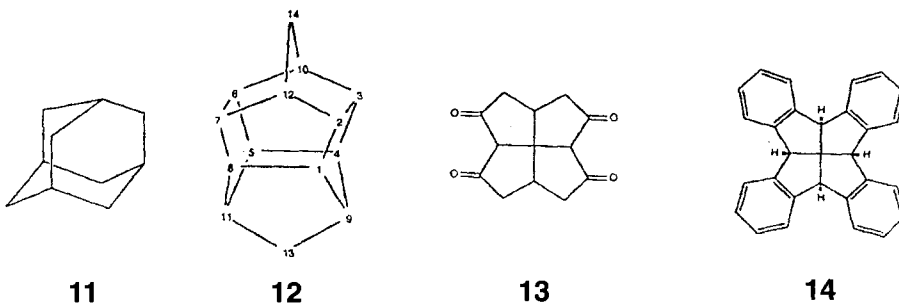
c) Constrained at the *ab initio* value.

There are three nonequivalent C–C bonds in every five-membered ring of **2a** C(1)–C(2), C(2)–C(6), and C(6)–C(7). The three corresponding bond lengths are very similar, and it is not feasible to distinguish between them on the basis of the electron-diffraction data. A mean value $r_a = 1.5433 (3) \text{ \AA}$ was obtained. It was then decided to introduce the differences between the C–C bond lengths from the quantum-chemical calculations and use them as constraints in the structure analysis. The results are given in Table 2. Here the standard deviations of the least-squares refinement were obtained in a special calculation in which the C–C bond-length differences were also included among the variables. This allowed a more realistic error estimation for the individual C–C bond lengths as well as for the rest of the parameters. The bond lengths (r_g) and bond angles with estimated total errors [11] are presented in Table 3.

Table 3. Bond Lengths r_g [\AA] and Bond Angles [deg] of all-cis-[5.5.5.5]Fenestrane (**2**) with Estimated Total Errors from Gas-Phase Electron Diffraction at 349 K Nozzle Temperature

$(\text{C–H})_{\text{mean}}$	1.117 ± 0.003	C(2)–C(1)–C(3)	116.2 ± 0.5
$(\text{C–C})_{\text{mean}}$	1.545 ± 0.003	C(1)–C(2)–C(6)	105.4 ± 0.3
C(1)–C(2)	1.558 ± 0.005	C(6)–C(2)–H(14)	110.8 ± 1.8
C(2)–C(6)	1.539 ± 0.008	C(2)–C(6)–H(18)	108.9 ± 0.9
C(6)–C(7)	1.542 ± 0.013	C(2)–C(6)–H(19)	102.2 ± 1.0
		C(2)–C(1)–C(5)	106.2 ± 0.2
		C(2)–C(6)–C(7)	103.7 ± 0.2
		C(1)–C(2)–H(14)	106.7 ± 4.2

Discussion. – Several structural features are apparent from the electron-diffraction analysis. As anticipated from its sterically crowded environment, the C–C bonds involving the central C-atom C(1) of **2a** are longer than those at the periphery (*cf.* Table 3²). This corroborates the well known results found for tri(*tert*-butyl)methane (= 3-(*tert*-butyl)-2,2,4,4-tetramethylpentane; (*t*-Bu)₃CH) where the central C–C bond length r_g is 1.611 (5) Å and the terminal one 1.548 (2) Å [15]. The C(1)–C(2) bond in **2a** is, however, longer than that of neopentane (= 2,2-dimethylpropane; Me₄C; r_g = 1.539 (3) Å) [16]. The C(2)–C(6) bond in **2a** might be compared with that of adamantane [17] (**11**) where the bond length r_g = 1.542 (2) Å is very precisely determined because of the high symmetry of the molecule, or with the corresponding *C(tert)*–*C(sec)*, bond length in the heptacyclic tetradecane **12** which contains four nonequivalent types of C–C bonds (r_g : C(1)–C(8) = 1.586 (4), C(1)–C(2) = 1.528 (6), C(1)–C(9) = 1.553 (4), and C(9)–C(13) = 1.532 (4) Å) [18].



The C(6)–C(7) bond of **2a** should probably be best compared to the bond length of cyclopentane (r_g = 1.546 (1) Å) [19]. Considering the estimated experimental errors, the two C–C bonds at the periphery of **22** are hardly distinguishable, while the central C–C bond appears to be distinctly longer than the two others.

The rather long mean C–H bond (r_g = 1.117 (3) Å) of **2a** is consistent with those found in similar molecules (*cf.* Table 4).

Table 4. Mean r_g (C–H) Bond Lengths in Fenestrane **2** and Related Molecules

Compound	r_g (C–H)	Ref.
Me ₄ C	1.119 (8) ^{a)}	[16a]
	1.125 (3)	[16b]
(<i>t</i> -Bu) ₃ CH	1.111 (3)	[15]
Adamantane (11)	1.117 (4)	[17]
Cyclopentane	1.114 (2)	[18]
Heptacyclic tetradecane 12	1.117 (3) ^{a)}	[19]
2	1.117 (3)	present work

^{a)} r_a was converted to r_g .

²⁾ A short C–C single bond in a sterically crowded situation was found in the X-ray structure analysis of tetra(*tert*-butyl)tetrahedrane (= tetra(*tert*-butyl)tricyclo[1.1.0.0^{2,4}]butane) [13]. Recent MM3 calculations suggested a very short C–C single bond for hexa(*tert*-butyl)bitetrahydridyl [14].

The fact that two of the opposite bond angles in the central $C(C)_4$ fragment are larger than the four remaining ones (*cf.* Table 3) is a clear indication for the unique structural feature of the fenestranes. The bond angles $C(2)-C(1)-C(3)$ ($116.2 \pm 0.5^\circ$) and $C(2)-C(1)-C(5)$ ($106.2 \pm 0.2^\circ$) are similar to those found for all-*cis*-[5.5.5]fenestrane-tetrone **13** by X-ray structure analysis [5]. Whereas the 1H - and ^{13}C -NMR data of **2** at room temperature are interpreted in terms of an apparent D_{2d} symmetry, the electron-diffraction analysis clearly shows the absence of planes of symmetry. The cyclopentane rings adopt a twist-envelope (half-chair) conformation in such a way that the structure is close to D_2 symmetry. This conformational preference is different from that found for tetrone **13** by X-ray structural analysis, where two adjacent cyclopentanone units adopt an envelope and the two others a twist-envelope form [5] [20]. The torsional angle $C(3)-C(1)-C(2)-H(14)$ of **2a** is 12.4° . Since this value applies to all four torsional angles across the central quaternary C-atom, it is evident that the four bridgehead H-atoms prefer synclinal rather than eclipsic positions, consistent with the apparent D_2 symmetry of **2a**. Evidence for non-ecliptic locations of the bridgehead H-atoms was also found in the X-ray structure analysis of tetrone **13** [5]. The D_2 symmetry of **2a** is unique, since the benzo-annulated fenestrane **14** prefers a structure with S_4 symmetry in the solid state [20]. Also, the NMR data of **14**, bearing four bridgehead substituents are interpreted in terms of two S_4 conformers which interconvert at different rates [21]. Finally, it should be mentioned that *ab initio* calculations (RHF/6-31G*) for **2** clearly indicate a structure which closely resembles **2a** [22].

Concluding Remarks. – An efficient synthesis of the parent all-*cis*-[5.5.5]fenestrane (**2**) in sufficient amount is reported, allowing the elucidation of its structure by electron diffraction. The four cyclopentane rings adopt twist-envelope (half-chair) conformations, and the four bridgehead H-atoms are in non-ecliptic positions. The symmetry of **2a**, best described by D_2 , suggests two conformers which interconvert at an unknown but most likely rather high rate.

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Experimental Part

General. The solvents EtOH, $CDCl_3$, and pyridine were *puriss. grade* (Fluka); benzene and toluene were *purum* grade and distilled over P_2O_5 . The reagents used were from Fluka: Raney-Ni (*puriss.*), ethane-1,2-dithiol (*purum*), 1-hydroxypyridine-2(1*H*)-thione (*purum*), and $BF_3 \cdot Et_2O$ (*pract.*). All reactions were performed under N_2 . If not stated otherwise, the crude reaction product was extracted with Et_2O , the extract washed with NaCl soln. dried ($MgSO_4$), and evaporated. In most cases, the residue was chromatographed over SiO_2 (silica gel for flash chromatography (FC), 30–60 μm ; J. T. Baker). TLC: alu plates 60 F_{254} , Merck. GC: Carlo-Erba instrument; SE 54 (20 m), either isothermic or with a temp. program (100–200°, 3°/min); HP-5 (25 m, 0.2 mm) with, H_2 (1.0 bar), at injection temp. 220°. M.p.: Büchi SMB-20; uncorrected. IR: Perkin-Elmer PE 782; in cm^{-1} ; $CHCl_3$ solns.; 0.2-mm cells. NMR: Bruker-AM-400, -AM-300, or Varian-EM-360-L spectrometers; in $CDCl_3$; chemical shifts δ in ppm rel. to internal Me_4Si ($= 0$ ppm), coupling constants J in Hz, multiplicities from DEPT. MS: Varian MAT CH 7A, ionisation energy 70 eV; in m/z (rel. intensity in %). GC/MS: Se-54 (26 m, 0.3 mm), with He (0.9 bar), at injection temp. 220°; Varian Mat 445; scan time 1.3 s.

Ethyl 9-Oxotetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-1-carboxylate (6). A soln. of oily acid **3** [6] (2 g, 6.53 mmol) in toluene (56 ml) was slowly added to a stirred suspension of **5** (4 g, 20.09 mmol) in toluene (143 ml) at r.t. After 5 min, pyridine (3.09 g, (3.87 mmol)) was added and the mixture heated to 80° for 5 h. The cooled orange soln. was decanted and the toluene distilled off. The brown residue was dissolved in EtOH (120 ml) and refluxed with a large excess of Raney-Ni overnight. After filtration of the cooled mixture over *Celite* and washing with EtOH and H₂O, the filtrate was extracted with Et₂O. Workup and chromatography (hexane/Et₂O 1:1) gave 0.62 g of **6**, 0.176 g of **7**, and 0.174 g of **4d**. Yield of **6/7**, 47%.

6: *R*_f (hexane/Et₂O 1:1) 0.39. GC (*HP* 5; 160°, isotherm): *t*_c 12.07 min. IR: 1720s. ¹H-NMR: 1.26 (*t*, 3 H); 1.24–1.44 (*m*, 2 H); 1.58–1.75 (*m*, 3 H); 1.86–1.99 (*m*, 2 H); 2.30–2.44 (*m*, 2 H); 2.47–2.58 (*m*, 2 H); 4.03–4.23 (*m*, 2 H). ¹³C-NMR: 14.6 (*q*); 29.14 (*t*); 30.60 (*t*); 33.29 (*t*); 35.20 (*t*); 36.73 (*t*); 42.59 (*d*); 44.18 (*t*); 54.79 (*d*); 60.41 (*t*); 61.39 (*d*); 64.45 (*s*); 75.02 (*s*); 176.25 (*s*); 206.57 (*s*).

Ethyl 9α,β-Hydroxytetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-1-carboxylate (7): *R*_f (hexane/Et₂O 1:1) 0.28. GC (*HP* 5; 160°, isotherm): *t*_R 11.32 min. IR: 3620w, 3520w, 1710s. ¹H-NMR: 1.28 (*t*, 3 H); 1.30–2.25 (*m*, 17 H); 2.35 (*m*, 1 H); 3.76–3.83 (*m*, 0.6 H); 4.12 (*q*, 2 H); 4.08–4.22 (*m*, 0.4 H). GC-MS: 264 (1, *M*⁺), 218 (37), 200 (20), 190 (28), 188, 173 (34), 172 (52); 160 (63). *4β*-(Ethoxycarbonyl)tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-2β,12β-carbolactone (**4d**): *R*_f (hexane/Et₂O 1:1) 0.10. GC (*HP*-5; 100–200°, 3°/min): *t*_R 26.53 min. IR: 1770s; 1720s. ¹H-NMR: 1.19–1.38 (*m*, 4 H); 1.41–1.60 (*m*, 2 H); 1.64–1.94 (*m*); 2.01–2.1 (*m*, 1 H); 2.30–2.42 (*m*, 3 H); 2.45–2.54 (*m*, 1 H); 2.97–3.01 (*dd*, 1 H); 3.13–3.21 (*m*, 2 H); 4.10–4.18 (*m*, 2 H); 4.95–4.99 (*dd*, 1 H). ¹³C-NMR: 13.95 (*q*); 31.15 (*t*); 31.38 (*t*); 37.87 (*t*); 41.58 (*t*); 43.24 (*t*); 47.37 (*d*); 49.44 (*d*); 55.00 (*d*); 60.11 (*d*); 60.84 (*t*); 64.57 (*s*); 82.90 (*s*); 86.23 (*d*); 175.53 (*s*); 179.67 (*s*). GC-MS: 290 (17, *M*⁺), 244 (39), 216, 188 (33), 171 (32), 144 (22), 130 (52), 117 (39), 105 (26), 91 (39).

5-Oxotetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-1β-carboxylic Acid (8). At 0°, **6/7** (0.662 g, 2.52 mmol) was reduced with LiAlH₄ (0.238 mg, 6.2 mmol) in Et₂O for 3 h. The crude diol (0.541 g, 2.44 mmol) was oxidized with Jones reagent in acetone (180 ml); 0.479 g (84%) of **8**. M.p. 125°. IR: 1730s, 1695s. ¹H-NMR: 1.31–1.41 (*m*, 2 H); 1.61–1.76 (*m*, 3 H); 1.88–2.00 (*m*, 2 H); 2.03–2.18 (*m*, 4 H); 2.21–2.24 (*m*, 1 H); 2.32–2.42 (*m*, 3 H); 2.49–2.56 (*m*, 1 H); 2.64 (*dd*, 1 H). ¹³C-NMR: 29.21 (*t*); 30.76 (*t*); 33.06 (*t*); 36.75 (*t*); 37.31 (*t*); 42.78 (*t*); 44.15 (*t*); 54.96 (*d*); 61.41 (*d*); 64.47 (*s*); 75.35 (*s*); 182.84 (*s*); 222.7 (*s*). MS (45°): 234 (11, *M*⁺), 216 (16), 188, 160 (74), 117 (20), 105 (16), 91 (27).

Tricyclo[5.5.1.0^{4,13}.0^{10,13}]tridecan-2-one (10). The acyl chloride, prepared from **8** (0.428 g, 1.82 mmol) by treatment with (COCl)₂ (0.91 ml, 10.54 mmol) and a trace of DMF in benzene (9 ml) for 2 h, was dissolved in toluene (2 ml) and slowly added to a suspension of **9** (0.238 g, 1.79 mmol) and pyridine (0.17 ml) in toluene (17 ml). This soln. was stirred overnight at 80°, decanted, and after removal of the toluene, refluxed in EtOH (16 ml) with an excess of Raney-Ni for 1.5 h. After workup and chromatography (hexane/Et₂O 1:1) 0.269 g (77%) of **10** was obtained. Colourless oil. *R*_f (hexane/Et₂O 1:1) 0.30. IR: 1730s. ¹H-NMR: 1.34–1.48 (*m*, 5 H); 1.57–2.06 (*m*, 7 H); 2.13–2.27 (*m*, 4 H); 2.33–2.38 (*m*, 1 H); 2.45–2.58 (*m*, 1 H). ¹³C-NMR: 30.11 (*t*); 31.75 (*t*); 31.75 (*t*); 31.88 (*t*); 32.30 (*t*); 34.40 (*t*); 43.63 (*t*); 45.78 (*d*); 53.31 (*d*); 54.16 (*d*); 60.20 (*d*); 70.53 (*s*); 222.2 (*s*). GC-MS: 190 (75, *M*⁺), 148 (37), 135 (46), 134 (46), 133 (42), 122 (50), 120 (57), 119 (40), 109 (65), 105 (48), 91, 57 (11), 55 (35), 53 (28), 43 (18), 41 (79).

cis-1-transoid-1,4-cis-4-transoid-4,7-cis-7-transoid-7,10-cis-10-transoid-10,1-Tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane (= all-cis-[5.5.5]Fenestrane; 2). A mixture of **10** (0.020 g, 0.105 mmol) and ethane-1,2-thiol (0.25 ml, 2.97 mmol) was treated with BF₃·Et₂O (0.069 ml, 0.105 mmol) for 30 min. After addition of MeOH and Et₂O, extraction with 10% NaOH soln. and workup, the crude thioketal was dissolved in EtOH (1.5 ml), treated with an excess of Raney-Ni, and heated to 60° for 2 h. After filtration through *Celite* and addition of H₂O, the org. phase was extracted with CFCl₃. After workup at 0°, the CFCl₃ was blown off with N₂ to give 15.5 mg (84%) of **2** as yellowish oil. Bulb-to-bulb distillation yielded colourless **2** (GC purity 99%) which solidified at 5–10°. GC (*HP*-5; 100°, isotherm): 6.98 min. IR: 2940s, 2910s, 2880m, 2860m, 1460m, 1452m, 1380w, 1365w, 1330w, 1305w. ¹H-NMR: 1.23–1.33 (*m*, 8 H); 1.62–1.77 (*m*, 9 H); 1.87–2.00 (*m*, 3 H). ¹³C-NMR: 31.08 (*t*); 52.15 (*d*); 53.57 (*d*); 73.43 (*s*). GC/MS: 177 (7); 176 (60, *M*⁺), 149 (12), 148, 134 (22), 133 (30), 120 (38), 107 (22), 106 (26), 105 (32), 93 (26), 91 (60), 80 (35), 79 (59).

The sample for the electron-diffraction analysis was prepared similarly from **10** (0.4 g, 2.1 mmol): 0.299 g (88%) of crude **2**. Bulb-to-bulb distillation from silica gel at 15 Torr/60° gave colourless **2** which was transferred into the ampoule with CFCl₃. After removal of the solvent by a flow of N₂ and gentle warming, the sample was 99% pure. GC (*HP*-5; r.t., isotherm, and after 17 min, 5°/min): 27.72 min.

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