First Evidence for a Carbon-Bridged [1.1]Ferrocenophane in the *anti* Conformation. Molecular Structure of *exo,exo,anti*-1,12-Dimethyl[1.1]ferrocenophane

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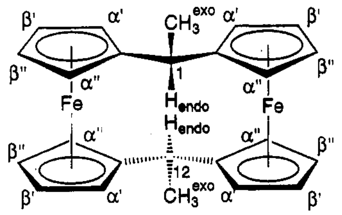
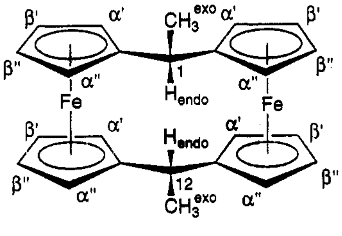
*Summary: A carbon-bridged anti-[1.1]ferrocenophane—exo,exo,anti-1,12-dimethyl[1.1]ferrocenophane (**1a**)—has been identified for the first time, and its molecular structure has been determined by X-ray diffraction. Stable anti conformers of carbon-bridged [1.1]ferrocenophanes have previously been ruled out because of steric strain.*

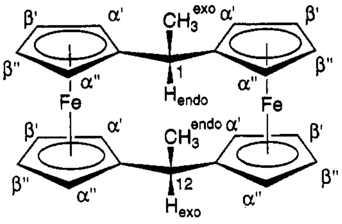
The possible existence of an *anti* conformation of [1.1]-ferrocenophanes (e.g. **1a**) in addition to the *syn* conformation (e.g. **1b**) has been debated since Watts published his first conformational investigation of [1.1]ferrocenophanes.[1] On account of expected severe steric crowding in the *syn* conformer **1b**, caused by nonbonded intramolecular interactions of the methine hydrogens and the α-hydrogens, respectively, Watts suggested a twisted *anti* conformation for 1. However, later X-ray diffraction studies have shown that the major product from the synthesis of 1,12-dimethyl[1.1]ferrocenophane (**1**) has a twisted *syn* conformation, i.e. a twisted **1b** structure.[2,3] Mueller-Westerhoff *et al.*[4] have pointed out that *anti*-[1.1]ferrocenophanes have never been observed since they would be completely rigid and sterically very unfavorable (due to repulsion between the inner α-protons). However, the bis(di-*n*-butylstannyl)-bridged analogue of 1 has been shown to exist in the *anti* conformation.[5] Another product from the synthesis of 1 was identified as an isomer of **1b**, and the structure *exo,endo,syn*-1,12-dimethyl[1.1]ferrocenophane (**1c**) was proposed, but no structural proof was given.[6,7]



1a



1b



1c

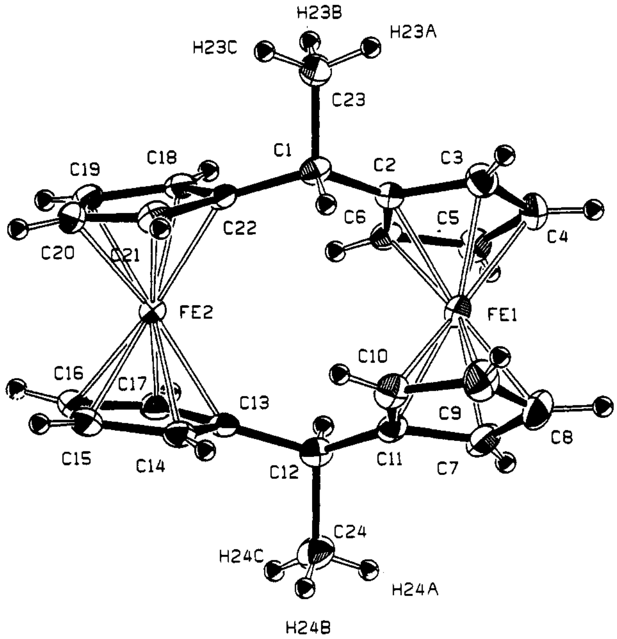


Figure 1. Computer-generated plot of **1a**, showing the crystallographic numbering. Selected bond distances (Å) and angles (deg) are as follows: Fe1–Fe2 = 4.604(1), Fe1–C2 = 2.032(3), Fe1–C4 = 2.052(4), Fe1–C9 = 2.043(4), Fe1–C11 = 2.034(3), Fe2–C13 = 2.105(3), Fe2–C16 = 2.027(4), Fe2–C20 = 2.033(3), Fe2–C22 = 2.100(3), C1–C2 = 1.507(4), C1–C22 = 1.511(4), C1–C23 = 1.542(5), C2–C3 = 1.438(5), C3–C4 = 1.421(5), C20–C21 = 1.412(5), C21–C22 = 1.412(5), C2–C1–C22 = 116.9(3), C2–C1–C23 = 109.5(3), C11–C12–C13 = 118.1(3), C11–C12–C24 = 109.2(3).

These findings led us to investigate the structure and reactivity of isomers of 1. Taking advantage of the progress

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(1) Watts, W. E. *J. Am. Chem. Soc.* **1966**, *88*, 855–856.

(2) McKechnie, J. S.; Berstedt, B.; Paul, I. C.; Watts, W. E. *J. Organomet. Chem.* **1967**, *8*, 29–31.

(3) McKechnie, J. S.; Maier, C. A.; Bersted, B.; Paul, I. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 138–143.

(4) Mueller-Westerhoff, U. T.; Nazzal, A.; Proessdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 7678–7681.

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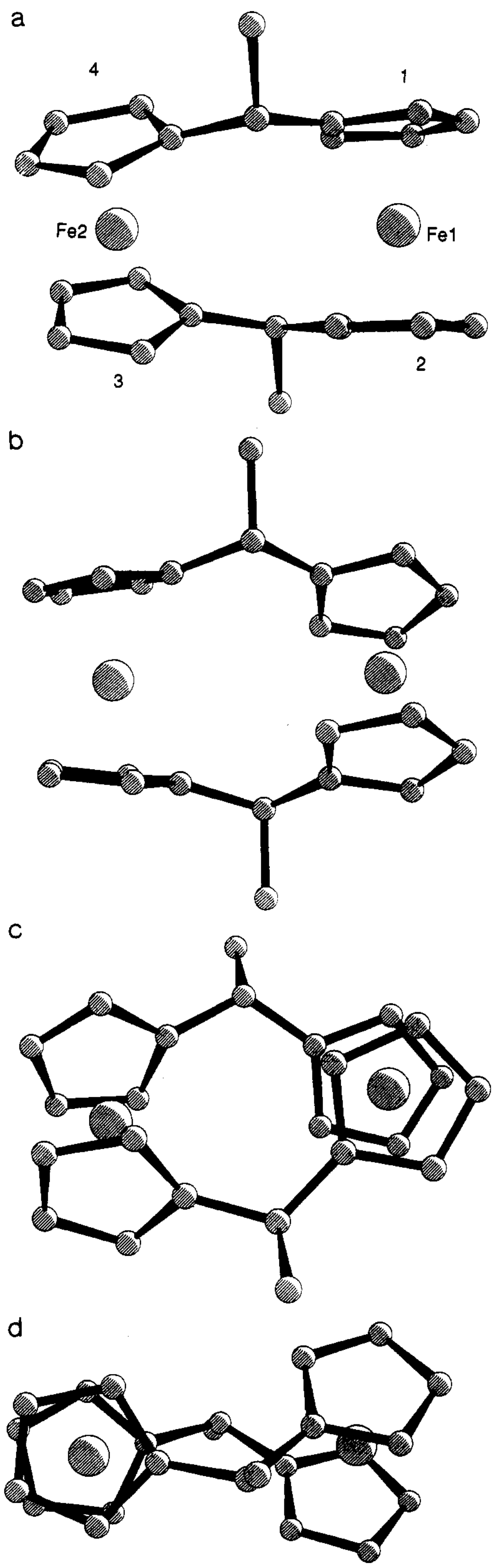

Figure 2. Computer-generated plots of **1a**, showing from top to bottom (a) the ring (plane) numbering, (b) the tilt angle for rings 3 and 4, (c) the extensive molecule twist and the *anti* conformation, and (d) the rotation angle for rings 3 and 4. The hydrogen atoms are omitted for clarity.

Table I. Twist Angles (deg) for Compounds 1a,b and 2a,b

	twist angle	
compd	planes 1 and 4	planes 2 and 3
1a (*anti*)	36.1	34.0
1b^{3} (*syn*)	30.2	31.5
2a^{a,5} (*syn*)	13.8	12.7
2b^{a,9} (*syn*)	1.6	3.2

[a] [1.1]Ferrocenophane (**2**) crystallizes in the two different phases **2a** and **2b**.[10]

Table II. Rotation Angles (deg) for Compounds 1a,b and 2a,b

	rotation angle	
compd	planes 1 and 2	planes 3 and 4
1a (*anti*)	3.4	53.9
1b^{3} (*syn*)	21.5	23.9
2a^{a,5} (*syn*)	~10	~10
2b^{a,9} (*syn*)	0.5	0.6

[a] Cf. footnote *a* in Table I.

Table III. Tilt Angles (deg) for Compounds 1a,b and 2a,b

	tilt angle	
compd	planes 1 and 2	planes 3 and 4
1a (*anti*)	4.1	22.7
1b^{3} (*syn*)	3.1	3.0
2a^{a,5} (*syn*)	2.4	1.4
2b^{a,9} (*syn*)	3.6	1.0

[a] Cf. footnote *a* in Table I.

Table IV. Bridge Angles (deg) for Compounds 1a,b and 2a,b

	bridge angle	
compd	around C1	around C12
1a (*anti*)	116.9(3)	118.1(3)
1b^{3} (*syn*)	117.5(8)	115.8(9)
2a^{a,5} (*syn*)	121.3(3)	121.7(3)
2b^{a,8} (*syn*)	121.8(3)	122.5(3)

[a] Cf. footnote *a* in Table I.

in the synthesis of **1a**, large amounts of the isomer (*vide supra*) have been produced and crystallized.[8] To our surprise, a crystal structure determination[9] shows that this isomer has a twisted *exo,exo,anti* structure (**1a**) and not the proposed *exo,endo,syn* structure (**1c**). The crystallographic numbering of the **1a** molecule is presented in Figure 1, and a complete visual description of the conformation, together with the plane numbering, is presented in the four views in Figure 2.

The conformational status of a [1.1]ferrocenophane may be described by twist, rotation, tilt, and bridge angles.[10] The bridge angle is defined as the bond angle around the bridging carbon with respect to the two quaternary ring carbons in the same organic ligand. The most striking feature is that the *anti* conformer **1a** exhibits the largest twist, rotation, and tilt angles, which strongly suggests that the alleged rigidity of the *anti* conformers should be reconsidered. It is clear that the large tilt angle between planes 3 and 4 (22.7°) is instrumental for the ability of the molecule to twist. Furthermore, a rotation angle of 53.9°

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(6) Barr, T. H.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1969**, *25*, 6001–6013.

(7) Cassens, A.; Eilbracht, P.; Nazzal, A.; Prössdorf, W.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1981**, *103*, 6367–6372.

(8) The preparation of compound **1a** was performed according to ref 7. Recrystallization was from hexane at room temperature while the hexane was evaporated slowly.

(9) Crystal data for **1a** at 153 K with Mo Kα (λ = 0.710 69 Å) radiation: $C_{24}H_{24}Fe_2$, a = 15.254(4) Å, b = 7.750(2) Å, c = 16.870(3) Å, β = 113.55(1)°, V = 1828.0(7) Å^3, ρ_{calc} = 1.541 g cm^{-3}, $\mu_{Mo\ K\alpha}$ = 15.91 cm^{-1}, fw 424.15, monoclinic, space group $P2_1/n$, Z = 4. The intensity data were collected at 150 K with ω–2θ scans and $2\theta_{max}$ = 50.0°. Full-matrix least-squares refinement on 2414 ($I > 3\sigma(I)$) reflections and 331 variables resulted in R = 0.030 (R_w = 0.036).

(10) Håkansson, M.; Löwendahl, M.; Davidsson, Ö.; Ahlberg, P. *Organometallics*, in press.

is reasonable only with reference to an undistorted [1.1]-ferrocenophane molecule, but for a comparison with ferrocene derivatives a value of 18.1° (72–53.9) is the adequate rotation angle. This angle is close to the ideal midpoint (18.0°) between an eclipsed and a staggered conformation, as can be seen from Figure 2d.

It has previously been assumed[11-13] that the degree of twist exhibited by a [1.1]ferrocenophane molecule is a reflection of the close intramolecular nonbonded contacts experienced by, primarily, the ring hydrogens. In **1a**, the shortest of these contacts are in the same range as the shortest intermolecular H···H contacts (2.28(5)–2.38(5) Å), which clearly indicates that packing effects cannot be disregarded when discussing conformational differences in the solid state.

The Fe–C bond distances vary between 2.027(4) and 2.105(3) Å, a relatively large interval which can be understood in terms of the extensive tilt in one of the "ferrocene units". The carbons in each cyclopentadienyl ring are essentially coplanar, the midpoints of rings 1 and 2 being slightly closer to Fe1 (1.64 Å) than the midpoints of rings 3 and 4 to Fe2 (1.67 Å). The Fe1–Fe2 intramolecular distance is 4.604(1) Å, and there is no indication of any metal–metal interaction. The bridge angles in **1a** are significantly smaller than for the parent compound **2**, where a widening of the bond angles at the bridging methylene carbons is a main factor in relieving internal steric overcrowding.[10]

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Supplementary Material Available: Tables of data collection parameters, positional and isotropic thermal parameters, full geometrical data, anisotropic thermal parameters for the non-hydrogen atoms, and least-squares planes and deviations therefrom (31 pages). Ordering information is given on any current masthead page.

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[11] Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702–717.

[12] Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 716–724.

[13] Singletary, N. J.; Hillman, M.; Dauplaise, H.; Kvick Å.; Kerber, R. C. *Organometallics* **1984**, *3*, 1427–1434.