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A *syn*-[1.1]Ferrocenophane with Approximate C_{2v} Symmetry

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Summary: The crystal structures of a new phase of [1.1]-ferrocenophane (1) and the monodeuterated analogue [1-^{2}H][1.1]ferrocenophane (2) have been determined by X-ray diffraction. The compounds are isostructural and crystallize in the monoclinic space group C2/c with Z = 8. Unit cell dimensions for compound 1 are a = 38.96(1), b = 7.498(6), c = 10.712(4) Å and β = 93.96(5)°. The structure was refined to a final R = 0.029 (R_w = 0.036) for 297 parameters and 1879 observed reflections. The molecule has the syn conformation, but exhibits remarkably little distortion with respect to the C_{2v} point group symmetry, despite H···H contacts of 2.04(4) and 2.13(5) Å. The rotation angles (cf. staggering) in the two "ferrocene units" are 0.5° and 0.6°, whereas the cyclopentadienyl rings are tilted 3.6° and 1.0° with respect to each other. The dihedral angles (i.e. twist angles) between the two cyclopentadienyl rings of the same organic ligand are 1.6° and 3.2°. The distance between the two iron atoms in the same molecule is 4.852(2) Å.

Introduction

[1.1]Ferrocenophanes have been suggested to exist as *syn*- and *anti*-conformers (*cf.* Figure 1), and unusual flexibility of *syn*-[1.1]ferrocenophane has been predicted from molecule mechanics models.[1] It has also been proposed that *syn*-[1.1]ferrocenophane undergoes a rapid degenerate rearrangement, in which *e.g.* the *exo*-methylene bridge hydrogens exchange with the *endo* hydrogens.[1] Evidence for such a pseudorotation mechanism has recently been obtained from dynamic NMR spectroscopy.[2] The molecular acrobatics disappear upon carbanion formation by treatment of *syn*-[1.1]ferrocenophane with butyllithium, which results in abstraction of one of the methylene bridge protons. For the ferrocenophanyl carbanion, no *exo*/*endo* hydrogen exchange could be detected by NMR spectroscopy.[3]

The interpretation of the above-mentioned results has been hampered by the lack of solid state structural information. For the parent compound, [1.1]ferrocenophane, a recent paper[4] reports of a twisted molecule in which the distortion from C_{2v} point group symmetry is explained by H···H steric repulsions. In the present paper we report the crystal structure of a new phase of *syn*-[1.1]ferrocenophane (1) together with that of its isotopologue [1-^{2}H][1.1]ferrocenophane (2), the latter being investigated in order to determine to what extent deuteration would result in conformational changes.

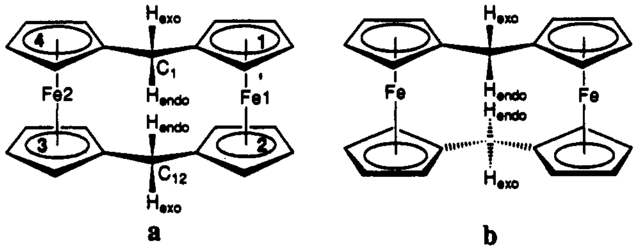

Figure 1. Diagrammatic representation of (a) a *syn*-[1.1]-ferrocenophane conformer and the plane numbering in 1 and (b) an *anti*-[1.1]ferrocenophane conformer.

Experimental Section

General Data. All operations were performed under argon using standard Schlenk techniques or on a high vacuum line. Tetrahydrofuran (THF) was distilled from sodium/benzophenone shortly prior to use.

Preparation of [1.1]Ferrocenophane and [1-^{2}H][1.1]-Ferrocenophane. [1.1]Ferrocenophane was synthesized, as described in the literature,[1b] from 1,1′-bis(6-fulvenyl)ferrocene. Single crystals for X-ray diffraction were prepared by dissolving 0.12 g of *syn*-[1.1]ferrocenophane in 5.0 mL of THF in a Schlenk tube at ambient temperature. The temperature of the solution was lowered very slowly to +4 °C, which resulted in the deposition of large plates of 1. Slow cooling was accomplished by inserting the Schlenk tube into a Dewar vessel at ambient temperature and thereafter storing the Dewar in a refrigerator for several days. [1-^{2}H][1.1]Ferrocenophane (2) was prepared according to the literature.[3b] Single crystals of X-ray quality were crystallized from a benzene solution of 2 at +4 °C. In contrast to earlier work,[4] we did not face any unusual problems in growing high quality single crystals of either compound.

X-ray Crystallography. Crystal and experimental data for compounds 1 and 2 are summarized in Table I. Full experimental details concerning compound 2 are given in the supplementary material. A crystal of 1 was mounted in a glass capillary, under argon, at −120 °C,[5] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The ω/2θ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Data were measured for $5 < 2\theta < 50°$ (+*h*,+*k*,±*l*) for a gold-yellow plate with approximate dimensions 0.40 × 0.30 × 0.20 mm, using an ω scan rate of 32 °/min and a scan width of

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Table I. Crystallographic Data for [1.1]Ferrocenophane (1) and [1-^{2}H][1.1]Ferrocenophane (2)

	1	2
formula	$C_{22}H_{20}Fe_2$	$C_{22}H_{19}DFe_2$
fw	396.09	397.10
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a, Å	38.96(1)	38.941(4)
b, Å	7.498(6)	7.497(4)
c, Å	10.712(4)	10.719(2)
α, deg	90	90
β, deg	93.96(5)	93.95(2)
γ, deg	90	90
V, Å^3	3122(3)	3122(2)
Z	8	8
d_{calc}, g/cm^3	1.685	1.689
μ, cm^{-1}	18.57	18.57
T, °C	−120	−120
R	0.029	0.030
R_w	0.036	0.037

Table II. Fractional Non-Hydrogen Atomic Coordinates and B_{eq} or *B* (Å^2) in [1.1]Ferrocenophane

atom	*x*	*y*	*z*	B_{eq}/B
Fe(1)	0.68734(1)	0.23053(7)	0.62430(4)	1.10(2)
Fe(2)	0.56510(1)	0.22947(7)	0.68525(5)	1.24(2)
C(1)	0.6243(1)	0.5150(5)	0.6205(3)	1.3(1)
C(2)	0.6552(1)	0.4352(5)	0.5646(3)	1.2(1)
C(3)	0.6891(1)	0.4987(5)	0.5985(4)	1.6(2)
C(4)	0.7130(1)	0.4121(5)	0.5232(4)	1.7(2)
C(5)	0.6938(1)	0.2946(5)	0.4422(3)	1.7(2)
C(6)	0.6582(1)	0.3079(5)	0.4660(3)	1.3(1)
C(7)	0.6714(1)	−0.0139(5)	0.6843(3)	1.3(2)
C(8)	0.7067(1)	−0.0201(5)	0.6555(4)	1.8(2)
C(9)	0.7249(1)	0.1056(5)	0.7331(4)	1.9(2)
C(10)	0.7013(1)	0.1897(5)	0.8087(3)	1.6(2)
C(11)	0.6679(1)	0.1171(5)	0.7791(3)	1.1(1)
C(12)	0.6375(1)	0.1660(5)	0.8518(3)	1.2(1)
C(13)	0.6013(1)	0.1140(5)	0.8100(3)	1.5(2)
C(14)	0.5723(1)	0.1786(6)	0.8726(4)	1.9(2)
C(15)	0.5421(1)	0.0937(5)	0.8217(4)	2.2(2)
C(16)	0.5515(1)	−0.0247(6)	0.7268(5)	2.4(2)
C(17)	0.5880(1)	−0.0129(5)	0.7193(4)	2.1(2)
C(18)	0.5754(1)	0.3093(6)	0.5088(4)	2.0(2)
C(19)	0.5390(1)	0.2966(6)	0.5191(4)	2.1(2)
C(20)	0.5298(1)	0.4132(5)	0.6150(4)	1.9(2)
C(21)	0.5604(1)	0.4984(5)	0.6643(4)	1.7(2)
C(22)	0.5890(1)	0.4346(5)	0.5989(3)	1.2(1)

Table III. Selected Intramolecular Distances (Å) and Angles (deg) in [1.1]Ferrocenophane

Fe(1)–C(2)	2.055(4)	C(1)–C(2)	1.505(5)
Fe(1)–C(3)	2.031(4)	C(1)–C(22)	1.503(5)
Fe(1)–C(4)	2.042(4)	C(11)–C(12)	1.505(5)
Fe(1)–C(5)	2.041(4)	C(12)–C(13)	1.504(5)
Fe(1)–C(6)	2.058(4)	C(2)–C(3)	1.428(5)
Fe(1)–C(7)	2.053(4)	C(3)–C(4)	1.429(5)
Fe(1)–C(8)	2.043(4)	C(4)–C(5)	1.414(6)
Fe(1)–C(9)	2.036(4)	C(5)–C(6)	1.428(5)
Fe(1)–C(10)	2.036(4)	C(6)–C(2)	1.435(5)
Fe(1)–C(11)	2.055(4)	C(7)–C(8)	1.431(5)
Fe(2)–C(13)	2.064(4)	C(8)–C(9)	1.416(5)
Fe(2)–C(14)	2.043(4)	C(9)–C(10)	1.414(5)
Fe(2)–C(15)	2.038(4)	C(10)–C(11)	1.428(5)
Fe(2)–C(16)	2.035(4)	C(11)–C(7)	1.426(5)
Fe(2)–C(17)	2.047(4)	H(1B)···H(12A)	2.50(5)
Fe(2)–C(18)	2.048(4)	H(6)···H(18)	2.04(4)
Fe(2)–C(19)	2.051(4)	H(6)···H(7)	3.28(5)
Fe(2)–C(20)	2.053(4)	H(6)···H(17)	3.34(5)
Fe(2)–C(21)	2.036(4)	H(7)···H(17)	2.13(5)
Fe(2)–C(22)	2.052(4)	Fe(1)···Fe(2)	4.852(2)

C(2)–C(1)–C(22)	121.8(3)	C(1)–C(2)–C(6)	131.8(3)
C(2)–C(1)–H(1A)	108(2)	C(3)–C(2)–C(6)	106.7(3)
C(2)–C(1)–H(1B)	110(2)	C(2)–C(3)–C(4)	109.4(3)
C(11)–C(12)–C(13)	122.6(3)	C(3)–C(4)–C(5)	107.0(3)
C(11)–C(12)–H(12A)	109(2)	C(4)–C(5)–C(6)	109.0(3)
C(11)–C(12)–H(12B)	107(2)	C(5)–C(6)–C(2)	108.0(3)
C(1)–C(2)–C(3)	121.2(3)		

(1.31 + 0.30 tan θ)°. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections monitored regularly after measurement of 150 reflections indicated crystal stability during data collection. Correction was made for Lorentz and polarization effects. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.88 to 1.00. Of the 2963 unique reflections measured, 1879 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 24 reflections in the range $46.8 < 2\theta < 49.8°$.

The structure was solved by direct methods (MITHRIL[6]). Full-matrix least-squares refinement, including anisotropic thermal parameters for the iron and carbon atoms and isotropic thermal parameters for the hydrogen atoms, gave a final $R = 0.029$ ($R_w = 0.036$) for 297 parameters and 1879 observed reflections. The maximum and minimum values in the final difference map were 0.31 and −0.46 e/Å^3, respectively. Reflections were weighted according to $w = [\sigma^2(F_0)]^{-1}$.

All calculations were carried out with the TEXSAN[7] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 8. Structural illustrations have been drawn with ORTEP.[9] Final positional parameters are listed in Table II and selected interatomic distances and angles in Table III.

Results and Discussion

Since compounds 1 and 2 are isostructural, the following discussion will focus on the structure of [1.1]ferrocenophane, and initially the three following angles are defined: the tilt angle, the twist angle, and the rotation angle. The *tilt angle* is defined as the dihedral angle between the best planes of the two cyclopentadienyl rings (see Figure 1a for the numbering of planes) of one "ferrocene unit". In 1, these angles are 3.6° (planes 1 and 2) and 1.0° (planes 3 and 4), which, in comparison with literature data[10] for a large number of ferrocene derivatives, are significantly low values. The term twist has, by different authors,[1d,10–12] been used to represent two separate kinds of distortion. In order to avoid confusion, we would like to suggest that the *twist angle* be defined by the dihedral angle between the best planes of the cyclopentadienyl rings of the same organic ligand. The angles of twist for the organic ligands (*viz.* the dihedral angle between planes 1 and 4 and the dihedral angle between planes 2 and 3) in 1 are 1.6° and 3.2°, respectively, thus reflecting the small amount of distortion from C_{2v} point group symmetry. Finally, the term *rotation angle* is reserved for the meaning given by Churchill and Wormald[10] in their compilation of angles of rotation and tilt for ferrocene derivatives, *i.e.* for [C–(center of gravity of ring 1)–(center of gravity of ring 2)–C] torsion angle, which is illustrated in Figure 2. In 1, the angles of rotation are 0.5° (rings 1 and 2) and 0.6° (rings 3 and 4). A

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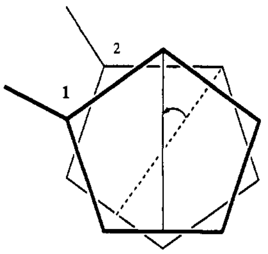

Figure 2. Rotation angle for the hypothetical planes 1 and 2.

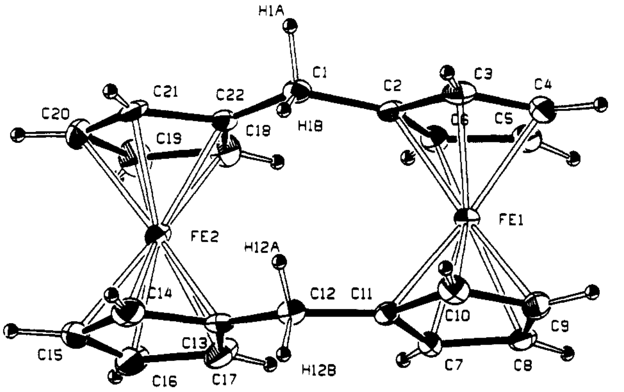

Figure 3. Crystallographic numbering in *syn*-[1.1]ferrocenophane. Each hydrogen atom has the same numeral as the carbon to which it is attached.

qualitative estimate of the small amount of distortion in 1 from the C_{2v} conformation is visualized in Figure 3, and the stereoscopic drawing in Figure 4 emphasizes this point even further. This approximate C_{2v} conformation contrasts to the recently reported *syn*-[1.1]ferrocenophane molecular structure,[4] where a substantial twist (13.8° and 12.7°) also is reflected in rotation angles of approximately 10°. In *syn*-1,12-dimethyl[1.1]ferrocenophane, the angles of tilt are 3.1° and 3.0°, the twist angles are 30.2° and 31.5° and the rotation angles are 21.5° and 23.9°.[12] 2,2′-Trimethylene[1.1]ferrocenophane and 3,3′-trimethylene-[1.1]ferrocenophane exhibit lower values of twist and tilt (ranging from 2–14°),[11] but in these molecules the trimethylene bridges inhibit the rotation of the rings and, consequently, the twisting is also restricted.

It has previously been assumed[1d,11,12] that the degree of twist exhibited by a [1.1]ferrocenophane molecule is a reflection of the close contacts experienced by some of the ring hydrogens. Specifically, referring to Figure 3, the H6···H18 and H7···H17 repulsions would be reduced by twisting one of the "ferrocene units" in relation to the other, until the H7···H18 or H6···H17 interactions become the dominant steric factors. It has been suggested[13] that it is the latter interactions that actually determine the angle of twist. In contrast to these assumptions, the present work demonstrates short H6···H18 (2.04 Å) and H7···H17 (2.13 Å) distances but almost no twisting. On the other hand, the C–CH_2–C bond angles at the bridging methylene carbons differ considerably (121.8(3)° and 122.6(3)°) from the tetrahedral angle, which illustrates an alternative mechanism for reducing the internal steric overcrowding. The corresponding C–CH_2–C bond angles in *syn*-1,12-dimethyl[1.1]ferrocenophane[12] are significantly smaller, *viz* 117.5(8) and 115.8(9)°, since in this case, a twisting mechanism is instrumental in relieving internal steric strain.

Intramolecular bond lengths and angles are given in Table III. The Fe–C distances range from 2.031(4) to 2.064(4) Å and agree well with previous results.[4,10–12] The distances from the iron atoms to planes 1–4 do not differ significantly and vary only between 1.646 and 1.650 Å. The bridging methylene carbons are displaced approximately 0.13 Å (away from the iron atoms) from the planes of the cyclopentadienyl rings to which they are attached. The mean C–C distance in the four crystallographically independent cyclopentadienyl rings is 1.425 Å, which is somewhat longer than that found in ferrocene[14] (1.40 Å) and in 1,12-dimethyl[1.1]ferrocenophane[12] (1.41 Å), but the standard deviations (especially in the earlier work) prevent any decisive conclusions to be drawn from these data. Furthermore, in an electron diffraction study[15] the mean C–C distance in ferrocene was determined to be 1.431(5) Å, and an average value of 1.419 Å has been calculated[16] from X-ray studies on π-cyclopentadienyl compounds. The carbons in each cyclopentadienyl ring are essentially coplanar, the mean deviations from the least-squares planes varying from 0.0002 to 0.0020 Å. The mean internal C–C–C angle in the cyclopentadienyl rings is 108.0° (*cf.* Table III), which equals the ideal angle for a regular, planar pentagon. The Fe(1)···Fe(2) distance is 4.852(2) Å, which is considerably longer than the iron–iron distances in 1,12-dimethyl[1.1]ferrocenophane[12] (4.595(2) and 4.620(2) Å), a difference that can be explained by the distortion in the latter molecule, which brings the iron centers closer to each other. Furthermore, in the two 2,2′- and 3,3′-trimethylene[1.1]ferrocenophanes[11] in which one of the ferrocene units is bridged by a three-carbon bridge, which restricts distortion, the Fe···Fe distances are 4.74–4.77 Å and it is very likely that the variations in Fe···Fe distances for these [1.1]ferrocenophane molecules are ligand-induced and not related to any metal–metal bonding. On the other hand, metal–metal interactions have been suggested responsible for lowering the redox potential in [1.1]ruthenocenophane,[4] in which the solid state Ru···Ru distance is 4.701(1) Å.

In 1, there are eight identical [1.1]ferrocenophane molecules in the unit cell, each molecule lacking any crystallographic 2-fold rotation axis. Nevertheless, the low angles of tilt, twist, and rotation make it reasonable to describe 1 as having approximate C_{2v} point group symmetry. The packing pattern within the unit cell is displayed in a stereoscopic drawing (Figure 5), and the relevant intermolecular distances are given in Table IV. The closest H···H contacts between two different molecules are 2.34(5) and 2.43(5) Å, which should be compared to the previously mentioned intramolecular H···H contacts of 2.04(4) and 2.13(5) Å, when estimating to what extent packing effects have a significant impact on the molecular conformation.

It is evident that 1 exhibits a different conformation in this work compared to that of the molecule in the recently published paper.[4] Apart from the difference in twist and rotation angles, the two separate unit cells clearly indicates the existence of two different solid state phases of *syn*-[1.1]ferrocenophane, a possibility which is not contradicted by the conformational flexibility of the molecule. We were, however, not able to isolate any new phase by replacing

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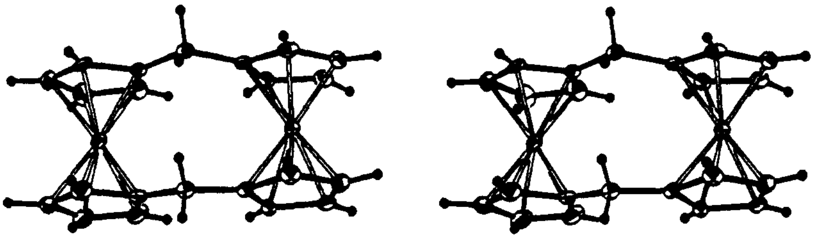

Figure 4. Stereoscopic view of the *syn*-[1.1]ferrocenophane molecule.

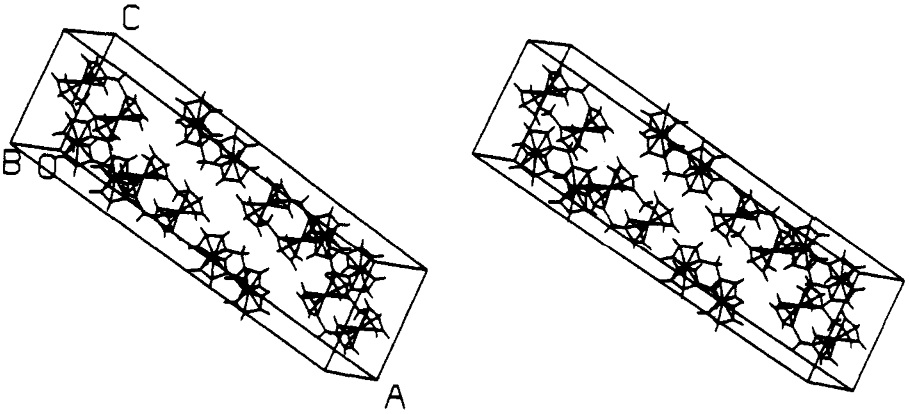

Figure 5. Stereoscopic drawing showing the packing pattern in a unit cell of 1.

Table IV. Intermolecular Contacts (Å) in 1 (less than 3.6 Å for C–C, 3.0 Å for C–H, and 2.5 Å for H–H)[a]

C(5)–C(7)^{i}	3.534(7)	C(20)–C(20)^{iii}	3.516(8)
C(15)–C(15)^{ii}	3.528 (9)		
C(2)–H(12A)^{iv}	2.99(4)	C(15)–H(15)^{ii}	2.82(4)
C(4)–H(10)^{iv}	2.87(4)	C(16)–H(15)^{ii}	2.95(4)
C(7)–H(5)^{v}	2.90(4)	C(16)–H(21)^{vi}	2.97(4)
C(7)–H(12B)^{i}	2.96(4)	C(20)–H(15)^{ii}	2.98(4)
C(8)–H(5)^{v}	2.91(4)	C(22)–H(14)^{iv}	2.97(4)
H(1A)–H(17)^{vii}	2.43(5)	H(20)–H(20)^{ii}	2.47(5)
H(7)–H(12B)^{i}	2.34(5)		

[a] Symmetry code: (*i*) $x, -y, z - {}^{1}/_{2}$; (*ii*) $1 - x, y, {}^{3}/_{2} - z$; (*iii*) $1 - x, 1 - y, 1 - z$; (*iv*) $x, 1 - y, z - {}^{1}/_{2}$; (*v*) $x, -y, {}^{1}/_{2} + z$; (*vi*) $x, y - 1, z$; (*vii*) $x, 1 + y, z$.

a proton with a deutron at one of the bridge methylene groups. As mentioned above, compound **2**, [1-^{2}H][1.1]-ferrocenophane, is isostructural with **1** (*cf.* Table I), and bond distances and angles do not differ significantly from those in **1**. Full data on compound **2** is available in the supplementary material.

In conclusion, it is evident that—in this *syn*-[1.1]-ferrocenophane phase—the "overcrowding effect" experienced by the inner protons in the 2-position is primarily reduced by an increase in the C–CH$_2$–C bond angles, rather than by relaxation from a C_{2v} conformation, induced by molecule twisting. Furthermore, this work has indicated the existence of two solid state *syn*-[1.1]ferrocenophane isomers, separated merely by a twist of about 10°.

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Supplementary Material Available: Compounds **1** and **2**: tables of H-atom coordinates, anisotropic thermal parameters for the non-hydrogen atoms, and full geometrical data. Compound **2**: crystallographic and experimental details, tables of positional and isotropic thermal parameters (55 pages). Ordering information is given on any current masthead page.

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