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Isomorphism and phase transition in triferrocenylboroxine and triferrocenylborazine

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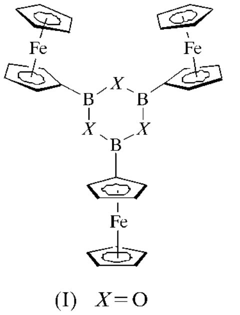
The crystal structures of triferrocenylboroxine, $[Fe_3(C_5H_5)_3(C_{15}H_{12}B_3O_3)]$, (I), and triferrocenylborazine, $[Fe_3(C_5H_5)_3(C_{15}H_{15}B_3N_3)]$, (II), are isomorphous. At room temperature, the space group is $Cmc2_1$ and the molecules have crystallographic m symmetry. A reversible phase transition occurs at 283 (2) K for (I) and at 263 (5) K for (II). In the low-temperature phase, the space group of both compounds is $P2_1$ and the molecules no longer have internal symmetry. Intermolecular $C—H\cdots\pi$ interactions are enhanced in the low-temperature phase.

Comment

Polynuclear aggregates of transition metals are of great current interest. Ferrocene is a particularly well suited building block for the generation of redox-active oligomers due to its high chemical stability and unique electrochemical properties. Our group is currently exploring the potential of boron–nitrogen and boron–oxygen bonds for the facile synthesis of ferrocene-containing macromolecules (Jäkle *et al.*, 1995; Fontani *et al.*, 1998; Grosche *et al.*, 1999; Dinnebier *et al.*, 2000). In this context, compounds (I) and (II) have been prepared and investigated by X-ray crystallography. The crystal structures of (I) and (II) at room temperature are isomorphous. The molecules show crystallographic m symmetry; atoms Fe1, C11, C21, B1 and O2 (or N2) lie on a mirror plane (Figs. 1a and 1*b*). All three ferrocenyl substituents occupy the same side of the central six-membered ring. The molecules do not behave as rigid groups; the displacement parameters of the free five-membered rings are considerably larger than those of the B-substituted five-membered rings. Both molecules show larger than average displacement parameters in the direction normal to the mirror plane. The occurrence of large amplitude thermal motion is often found in the high-temperature phase of structures which undergo phase transitions.



(I) X=O
(II) X=NH

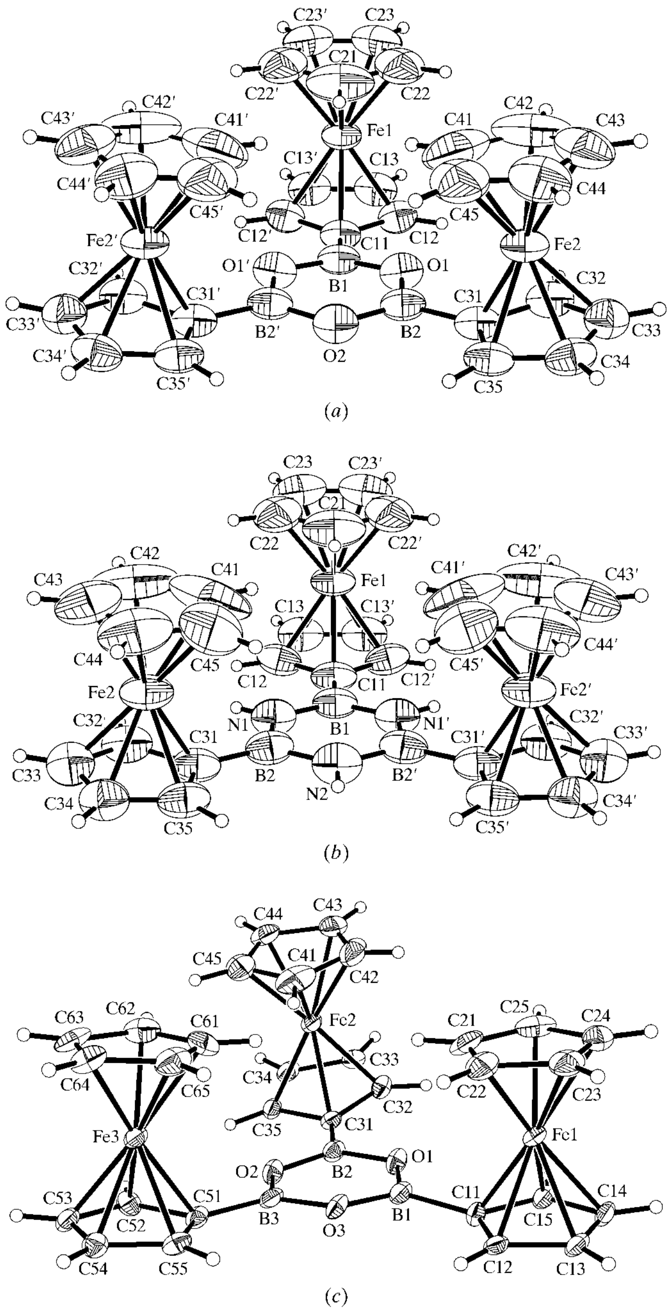


Figure 1
The molecular structure of (*a*) (I) at room temperature, (*b*) (II) at room temperature and (*c*) (I) at 154 K. Displacement ellipsoids are shown at the 50% probability level.

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The B—O bond lengths in (I) range from 1.376 (3) to 1.397 (3) Å, with an average value of 1.384 Å. Very similar B—O bond lengths, with an average of 1.381 Å, have been reported for other boroxines (Boese *et al.*, 1987; Brock *et al.*, 1987; Satoh & Cheng, 1994; Beckett *et al.*, 1997; Song *et al.*, 1993; Avent *et al.*, 1990). The B—N bond lengths in (II) range from 1.423 (6) to 1.442 (7) Å, with an average value of 1.431 Å. Similar B—N bond lengths, with an average value of 1.434 Å, have been reported for other borazines (Boese *et al.*, 1995; Viswamitra & Vaidya, 1965; Lux *et al.*, 1979). A B—N bond length of 1.431 Å has also been obtained from *ab initio* calculations on borazine (Kiran *et al.*, 2001). The B—N bond lengths in (II) are about 0.05 Å longer than the B—O bond lengths in (I).

The six-membered boroxine ring in (I) shows a small deviation from planarity; ring atoms O2 and B1 deviate by 0.061 (5) and 0.078 (4) Å, respectively, in the same direction from the O1/O1′/B2/B2′ plane. A smaller deviation from planarity is observed for the borazine ring in (II); ring atoms N2 and B1 deviate by only 0.037 (10) and 0.031 (10) Å, respectively, from the N1/N1′/B2/B2′ plane. The ferrocenyl groups are slightly tilted toward the center of the molecule. As a result, B1 deviates by 0.221 (6) Å from the C11/C12/C13/C12′/C13′ plane and B2 deviates by 0.203 (5) Å from the C31–C35 plane in (I). Corresponding values in (II) are 0.146 (13) Å for B1 and 0.149 (9) Å for B2. The five-membered rings of the ferrocenyl groups approximately have eclipsed conformations. A very similar molecular geometry has been observed in the crystal structure of triferrocenyltriselenatriborinane (Horn *et al.*, 1992); the tilting of the ferrocenyl groups toward the center of the molecule is even slightly more pronounced in this compound. There are no short intramolecular contacts in (I) and (II). The N—H groups of (II) cannot act as hydrogen-bond donors due to shielding by C—H bonds of the neighboring ferrocenyl groups. This forward shielding of the N—H and O groups is a requirement for the isomorphism of (I) and (II).

The crystal packing of (I) shows a weak intermolecular C—H···O interaction, with a H···O distance of 2.70 Å, and three intermolecular C—H···C(π) interactions, with H···C(π) distances of 2.70, 2.88 and 2.90 Å (Table 1 and Fig. 2). The crystal packing of (II) is similar. It shows a weak intermolecular C—H···N interaction, with a H···N distance of 2.75 Å, and three intermolecular C—H···C(π) interactions, with H···C distances of 2.78, 2.86 and 2.93 Å (Table 2). Intermolecular interactions with H···C distances exceeding 3.0 Å have not been included in Tables 1 and 2. The C—H donor groups do not point toward the centroids of the acceptor cyclopentadienyl rings. In contrast, they point closer to individual C atoms of those groups.

On cooling, both compounds undergo a reversible phase transition, (I) at 283 (2) K and (II) at 263 (5) K. Below the phase transition temperature, the crystal structures are monoclinic with space group $P2_1$. The low-temperature cells are related to the high-temperature cells by the transformation: $a_{\rm low} = 0.5a_{\rm high} - 0.5b_{\rm high}$, $b_{\rm low} = c_{\rm high}$ and $c_{\rm low} = -0.5a_{\rm high} - 0.5b_{\rm high}$. The loss of the mirror symmetry can result in twinning of the crystals. The twin domains in the low-temperature phase of (I) were found to be related by: $h' = -0.08h + 0.91l$, $k' = k$ and $l' = 1.09h + 0.08l$. This twin relation corresponds to the mirror plane of the high-temperature structure. The twin relations for the cell constants are identical to the relations found for the Miller indices *h, k* and *l*. The structure of (I) was determined at 154 K. The volume fraction of the twin domain refined to 0.209 (4). Only reflections belonging to the major domain were used for the structure refinement. *R* values and residual density of the low-temperature structure were larger than for the room-temperature structure as a result of the twinning. The largest

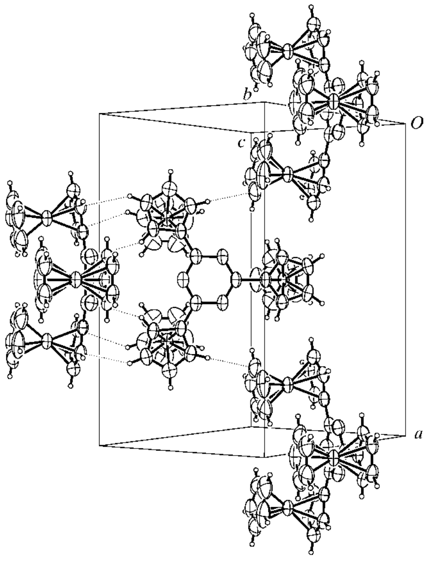

Figure 2
The crystal packing of (I) at room temperature viewed down $01\overline{1}$. Intermolecular C—H···O and C—H···C interactions are shown as dotted lines.

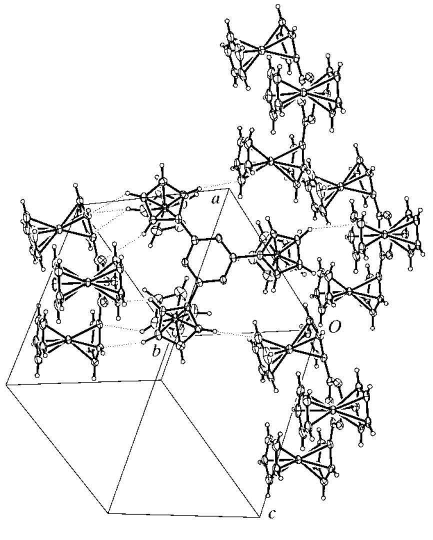

Figure 3
The crystal packing of (I) at 154 K with the view direction as in Fig. 2. Intermolecular C—H···O and C—H···C interactions are shown as dotted lines.

residual density was observed within 1 Å of the Fe atoms. The dimensions of the molecule at low temperature are similar to the room-temperature geometry. The B—O bond lengths range from 1.378 (8) to 1.388 (8) Å, with an average value of 1.383 Å. Also the deviation from planarity of the boroxine ring and the tilting of the ferrocenyl groups is as observed at room temperature. The structure of (II) at 100 K will be reported by Ma *et al.* (2002). The low-temperature phase of (II) again is isomorphous with the low-temperature phase of (I). Cell constants of (II) at 100 K are a = 11.046 (2), b = 10.316 (1), c = 12.040 (2) Å, β = 99.74 (1)° and V = 1352.2 (4) Å^3. The small crystal of (II) used by Ma *et al.* (2001) was cooled through the phase transition without occurrence of twinning. The larger crystal of (II) used in the present determination was seriously twinned in the low-temperature phase, resulting in poor net intensities. Thus, those data will not be given here.

The crystal packing of (I) at 154 K shows two weak intermolecular C—H⋯O interactions, with H⋯O distances of 2.64 and 2.79 Å, and nine intermolecular C—H⋯C interactions, with H⋯C distances less than 2.95 Å (Table 3 and Fig. 3). The intermolecular C—H⋯π interactions are clearly enhanced in the low-temperature phase. Displacement parameters at 154 K are reduced to about 40% of their room-temperature values. No larger than average displacement parameters are found for the low-temperature structure.

Experimental

The synthesis of (I) has been reported by Guo *et al.* (2001). Orange crystals suitable for X-ray analysis were obtained by evaporation at room temperature of a solution in chloroform. The synthesis of (II) will be reported by Ma *et al.* (2002). Orange crystals suitable for X-ray analysis were obtained by evaporation at room temperature of a solution in acetone.

Table 1
Hydrogen-bonding geometry (Å, °) for (I) at room temperature.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C32—H32⋯C43$^{\rm i}$	0.93	2.70	3.609 (5)	166
C34—H34⋯C32$^{\rm ii}$	0.93	2.88	3.653 (5)	142
C35—H35⋯O1$^{\rm ii}$	0.93	2.70	3.517 (4)	147
C44—H44⋯C35$^{\rm ii}$	0.93	2.90	3.676 (6)	142

Symmetry codes: (i) $\frac{1}{2}-x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, 2-y, \frac{1}{2}+z$.

Compound (I) at room temperature

Crystal data

$[Fe_3(C_5H_5)_3(C_{15}H_{12}B_3O_3)]$
M_r = 635.50
Orthorhombic, $Cmc2_1$
a = 17.643 (4) Å
b = 14.466 (2) Å
c = 10.481 (3) Å
V = 2675.1 (10) Å^3
Z = 4
D_x = 1.578 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 102 reflections
θ = 3–23°
μ = 1.64 mm^{-1}
T = 294 (2) K
Plate, orange
0.59 × 0.50 × 0.19 mm

Table 2
Hydrogen-bonding geometry (Å, °) for (II) at room temperature.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C32—H32⋯C43$^{\rm i}$	0.93	2.78	3.674 (10)	162
C34—H34⋯C32$^{\rm ii}$	0.93	2.93	3.695 (9)	140
C35—H35⋯N1$^{\rm ii}$	0.93	2.75	3.581 (7)	149
C44—H44⋯C35$^{\rm ii}$	0.93	2.86	3.687 (10)	148

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x, -y, z-\frac{1}{2}$.

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1996)
$T_{\rm min}$ = 0.346, $T_{\rm max}$ = 0.750
27 963 measured reflections
4607 independent reflections
3291 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.055
$\theta_{\rm max}$ = 32.4°
h = −25 → 25
k = −21 → 21
l = −15 → 15
330 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.108
S = 1.12
4607 reflections
184 parameters
H atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.52 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.37 e Å^{-3}
Absolute structure: Flack (1983), 2120 Friedel pairs
Flack parameter = 0.27 (2)

Compound (II) at room temperature

Crystal data

$[Fe_3(C_5H_5)_3(C_{15}H_{15}B_3N_3)]$
M_r = 632.55
Orthorhombic, $Cmc2_1$
a = 17.895 (3) Å
b = 14.792 (3) Å
c = 10.4806 (18) Å
V = 2774.3 (9) Å^3
Z = 4
D_x = 1.514 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 99 reflections
θ = 3–23°
μ = 1.57 mm^{-1}
T = 294 (2) K
Plate, orange
0.55 × 0.33 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1996)
$T_{\rm min}$ = 0.389, $T_{\rm max}$ = 0.885
15 621 measured reflections
3164 independent reflections
1953 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.095
$\theta_{\rm max}$ = 28.0°
h = −22 → 22
k = −19 → 19
l = −12 → 13
151 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.111
S = 1.11
3164 reflections
184 parameters
H atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 3.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ < 0.001
$\Delta\rho_{\rm max}$ = 0.40 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.44 e Å^{-3}
Absolute structure: Flack (1983), 1443 Friedel pairs
Flack parameter = 0.01 (4)

Table 3
Hydrogen-bonding geometry (Å, °) for (I) at 154 K.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C13—H13⋯C24$^{\rm i}$	0.95	2.91	3.733 (11)	145
C32—H32⋯C43$^{\rm ii}$	0.95	2.63	3.579 (12)	173
C34—H34⋯C55$^{\rm iii}$	0.95	2.83	3.686 (10)	151
C35—H35⋯O3$^{\rm iii}$	0.95	2.64	3.344 (8)	131
C44—H44⋯C51$^{\rm iii}$	0.95	2.94	3.576 (12)	126
C44—H44⋯C52$^{\rm iii}$	0.95	2.85	3.615 (12)	139
C52—H52⋯O1$^{\rm iii}$	0.95	2.79	3.674 (8)	155
C53—H53⋯C32$^{\rm iii}$	0.95	2.83	3.562 (10)	135
C55—H55⋯C64$^{\rm iv}$	0.95	2.68	3.586 (10)	159
C63—H63⋯C34$^{\rm iii}$	0.95	2.82	3.752 (11)	169
C63—H63⋯C35$^{\rm iii}$	0.95	2.83	3.608 (11)	140

Symmetry codes: (i) $-x, y-\frac{1}{2}, -1-z$; (ii) $-x, y-\frac{1}{2}, -z$; (iii) $1-x, \frac{1}{2}+y, -z$; (iv) $1-x, y-\frac{1}{2}, -1-z$.

Compound (I) at 154 K

Crystal data

$[Fe_3(C_5H_5)_3(C_{15}H_{12}B_3O_3)]$
M_r = 635.50
Monoclinic, $P2_1$
a = 10.896 (3) Å
b = 10.345 (4) Å
c = 11.709 (5) Å
β = 100.213 (18)°
V = 1298.9 (8) Å^3
Z = 2
D_x = 1.625 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 51 reflections
θ = 3–23°
μ = 1.69 mm^{-1}
T = 154 (2) K
Plate, orange
0.59 × 0.50 × 0.19 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1996)
$T_{\rm min}$ = 0.327, $T_{\rm max}$ = 0.733
27 634 measured reflections
8438 independent reflections
7048 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.114
$\theta_{\rm max}$ = 32.6°
$h = -15 \rightarrow 16$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
419 standard reflections frequency: 600 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.080
$wR(F^2)$ = 0.210
S = 1.25
8438 reflections
353 parameters
H atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 4.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 2.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.94 e Å^{-3}
Absolute structure: Flack (1983), 3800 Friedel pairs
Flack parameter = 0.16 (3)

The H atoms were taken from a difference Fourier synthesis. They were allowed for as riding atoms with fixed individual displacement parameters [U(H) = 1.2$U_{\rm eq}$(C) or U(H) = 1.2$U_{\rm eq}$(N)] using a riding model with fixed distances: H—N = 0.86 Å, H—C(aromatic) = 0.93 Å at room temperature and H—C(aromatic) = 0.95 Å at 154 K.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1093). Services for accessing these data are described at the back of the journal.

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