Spectroscopic Properties of Alkenylferrocenes; Crystal and Molecular Structure of (*Z*)-(1,2-Diphenylethenyl)ferrocene

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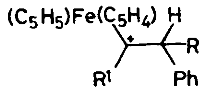
Studies of the ^{1}H n.m.r. and electronic spectra of a series of alkenylferrocenes, including (*E*) and (*Z*) stereoisomers of various styrylferrocenes, have provided methods of structure elucidation. Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 17.603(2)$, $b = 10.218(2)$, $c = 10.072(2)$ Å, $\beta = 103.27(2)°$. The structure has been determined by the heavy-atom method from diffractometer data and refined by full-matrix least-squares techniques to $R = 0.043$ for 2 219 unique reflections.

UPON treatment with a base (*e.g.* $[OH]^-$ or $[OR]^-$), ferrocenylcarbocations of the type (1) undergo deprotonation in preference to nucleophilic addition. In many cases, these reactions afford mixtures of stereoisomeric styrylferrocenes (2) and (3), which can usually be separated cleanly by preparative t.l.c. on SiO_2. In connection with a study[1,2] of the kinetics, stereochemistry, and mechanism of carbocation deprotonation and of the reverse process, a secure method of identification of the stereostructures of such (*E*),(*Z*)-isomeric alkenylferrocenes was required.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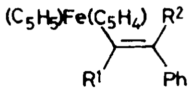
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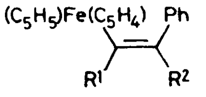
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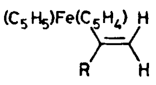
(a) $R^1 = R^2 = H$
(b) $R^1 = H$, $R^2 = Me$
(c) $R^1 = R^2 = Me$
(d) $R^1 = Ph$, $R^2 = Me$
(e) $R^1 = Ph$, $R^2 = H$

RESULTS AND DISCUSSION

Hydrogen-1 *N.M.R. Spectra.*—For styrylferrocenes of an (*E*),(*Z*) pair, straightforward structural assignment by ^{1}H n.m.r. spectroscopy is possible only for the parent system. Thus, the exclusive product of deprotonation of the cation (1a) can be assigned the (*E*) stereochemistry (2a) from the magnitude (*ca.* 16 Hz) of the vinylic proton coupling constant which is characteristic of a *trans*-disubstituted alkene.[3] Although the spectra of the alkenes of the other (*E*),(*Z*) pairs [(2),(3) b—e] show striking chemical-shift differences for the protons of equivalent types, immediate stereostructural assignments are not obvious. However, from a comparison of the spectra of a series of these and related alkenes of known stereochemistry, it is apparent that the ferrocenyl proton-resonance pattern provides a useful indication of the steric relationship of other groups (particularly phenyl) attached to the double bond. The ^{1}H n.m.r. spectra of the alkenes studied are in Table 1.

In the spectra of alkenylferrocenes of the types (4) and (5) (R = H, alkyl, or aryl), the protons of the substituted (C_5H_4) ferrocenyl ring give rise to an A_2B_2 pattern (often a pair of unsymmetrical, closely spaced, two-proton triplets) *downfield* of the singlet resonance of the unsubstituted (C_5H_5) ferrocenyl ring protons. In the spectra of the *gem*-diphenylvinyl derivatives (6a)—(6c), however, the C_5H_4-ring proton signals appear *upfield* of the C_5H_5-ring singlet with the shielding of two of these protons particularly marked. This shielding effect is due to the phenyl group situated *cis* to ferrocenyl in these alkenes since the *trans*-phenyl group of (2a) has no such influence. Surprisingly, the *gem*-phenyl group in the alkenes (4c) and (5c) has no differential effect on the shieldings of the neighbouring ferrocenyl protons; the C_5H_4 and C_5H_5 proton-resonance patterns for these alkenes are little different from those of alkyl analogues, *e.g.* (4b) and (5b).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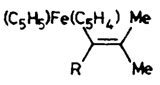
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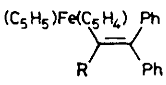
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(a) R = H
(b) R = Me
(c) R = Ph

This *cis*-phenyl shielding effect permitted identification of the stereostructures of the alkenes of the (*E*), (*Z*) pairs [(2),(3) b—d]. The spectra of the (*Z*)-alkenes (3b)—(3d) each contain a two-proton triplet upfield of the C_5H_5 singlet, whereas the C_5H_4-ring proton signals of their (*E*) isomers (2b)—(2d) appear downfield of the C_5H_5 singlet. The structures of the isomeric fused-ring alkenes (7) and (8) could be similarly identified. The spectrum of the former lacked upfield C_5H_3-ring proton resonances but contained a downfield one-proton triplet; the spectrum of the latter exhibited an upfield one-proton triplet, indicating the (*Z*) stereochemistry (8).

A less clear-cut structural differentiation was provided by the ^{1}H n.m.r. spectra of the (*E*),(*Z*) isomers (2e),(3e) since the C_5H_4-ring proton resonances for each appeared downfield of the C_5H_5 singlet. However, the ferrocenyl protons of one isomer were appreciably shielded relative to those of the other (Table 1), suggesting the (*Z*) stereochemistry (3e) for the former. This assignment, which

TABLE 1

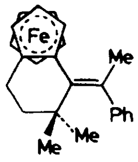
Chemical-shift values (τ) for alkenylferrocenes [a]

Compound	Ferrocenyl C_5H_5 [b]	Ferrocenyl $C_6H_{4(3)}$	Vinyl	Phenyl [c]	Methyl
(2a)	5.96	5.63(t) 5.83(t)	3.25, 3.35 (ABq) [d]	2.6—3.0	
(2b)	5.89	5.59(t) 5.76(t)	3.48(q) [e]	2.4—2.9	7.80(d)
(2c)	5.92	5.71(t) 5.85(t)		2.6—3.0	7.96(q) 8.09(q) [f]
(2d)	6.08	5.7— 5.95(m)		3.00(bs) 3.08(bs)	7.60(s)
(2e)	5.92	5.7— 5.8(m)	3.02(s)	2.63(bs) 2.8—3.2	
(3b)	6.06	6.08(m) 6.32(t)	3.90(q) [e]	2.80(bs)	7.97(d)
(3c)	6.03	6.13(t) 6.38(t)		2.6—3.0	7.82(q) 7.98(q) [f]
(3d)	6.08	6.10(m) 6.66(t)		2.70(bs) 2.6—2.8	8.30(s)
(3e)	6.18	5.9— 6.15(m)	3.48(s)	2.82(bs) 2.4—3.1	
(4b)	6.02	5.73(t) 5.92(t)	4.94(m) 5.24(m)		7.98(bs)
(4c)	6.02	5.78(t) 5.90(t)	4.58, 4.92 (ABq) [g]	2.6—2.9	
(5b)	5.86	5.8— 5.85(m)			7.96(bs) 8.25(bs) [h]
(5c)	6.02	5.8— 5.95(m)		2.5—2.9	7.98(s) 8.47(s)
(6a)	5.87	5.90(m) 6.16(m)	3.18(s)	2.4—2.8	
(6b)	5.92	5.98(t) 6.15(t)		2.75(bs) 2.7—3.1	7.85(s)
(6c)	5.96	6.16(t) 6.67(t)		2.6—3.2	
(7) [i]	6.02	5.68(t) 5.92(d)		2.6—3.0	7.59(s) 9.12(s) 9.44(s)
(8) [i]	6.12	6.10(m) 6.35(t)		2.6—3.0	7.89(s) 8.40(s) 8.75(s)

[a] For $CDCl_3$ solutions, with $SiMe_4$ as internal reference; s = singlet, bs = broadened singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] Singlet resonances. [c] Multiplets unless indicated otherwise. [d] *J ca.* 16 Hz. [e] *J ca.* 1.5 Hz. [f] *J ca.* 1.0 Hz. [g] *J ca.* 2.0 Hz. [h] Two coincident methyl signals. [i] The methylene proton signals appear as an AA′BB′ pattern at τ 7.5—7.8.

is in harmony with electronic-spectral correlations (see later), has been confirmed by an *X*-ray crystal-structure determination which is described in a later section.

The preferred conformation in solution of an (*E*)-styrylferrocene (9) allows π conjugation of the ferrocenyl and phenyl groups through a coplanar arrangement of the C_5H_4 ring, the double bond, and the Ph ring. For the (*Z*)-styryl isomers, however, steric repulsion between the C_5H_4 and Ph rings prevents coplanarity and causes either or both rings to twist from the double-bond plane * [*cf.* (10)]. Such distortion, which is clearly evident in the solid-state conformation of (3e) (see Figure 2), places the ferrocenyl C_5H_4 ring within the shielding volume, associated with the Ph ring, giving rise to the ^1H n.m.r. effects described earlier. It is apparent that phenyl out-of-plane twisting would be reinforced for compounds containing a geminal group other than hydrogen [*i.e.* (10; $R^2 \neq H$)] and this factor may be responsible for the differences noted earlier between the ferrocenyl proton shieldings for (3e) and those for the other (*Z*)-alkenes (3b)—(3d).



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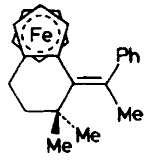

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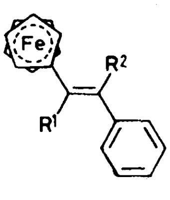

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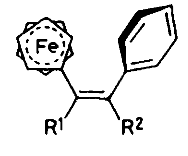

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Electronic Spectra.—The visible electronic-absorption spectra of 1-alkenylferrocenes contain a low-intensity band at *ca.* 450 nm which, although mainly *d–d* in character, is sensitive to double-bond substituent effects. An earlier study [5] showed that this absorption undergoes a bathochromic shift with modest intensification as π conjugation in the side chain is extended, *cf.* values for vinylferrocene and (2a). These and the corresponding values for the (*E*),(*Z*) isomers (2b)—(2e), (3b)—(3e) are in Table 2. For each (*E*),(*Z*) pair, the band intensity is significantly higher for the (*E*) isomer for which, as discussed earlier, more effective π conjugation through the styrylferrocene system is possible in solution. A similar situation occurs with (*E*)- and (*Z*)-1,2-diphenylethene (*i.e. trans-* and *cis*-stilbene, respectively); steric repulsion between the *cis*-phenyl groups of the latter leads to diminished π conjugation and an attendant lowering in intensity of the electronic-absorption bands compared with the corresponding values for the *trans* isomer.[6]

TABLE 2

Visible absorption bands for alkenylferrocenes *

Compound	$\lambda_{max.}$/nm	ε/dm³ mol⁻¹ cm⁻¹
Vinylferrocene	446	250
(2a)	455	1 000
(2b)	454	510
(2c)	455	490
(2d)	457	400
(2e)	462	700
(3b)	450	340
(3c)	451	320
(3d)	455	310
(3e)	456	300
(4c)	450	260

* For absolute EtOH solutions.

Crystal Structure of (Z)-(1,2-*Diphenylethenyl*)*ferrocene*.—In order to confirm the structure of the alkene (3e) and to establish the conformation in the solid state, the crystal structure was determined using *X*-ray

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* π-Conjugation of a double bond with a ferrocenyl group confers slightly greater stabilisation than that resulting from phenyl conjugation.[4]

TABLE 3

Bond lengths (Å)

Fe–C(1)	2.050(3)	C(9)–C(10)	1.406(6)
Fe–C(2)	2.031(3)	C(10)–C(6)	1.418(6)
Fe–C(3)	2.038(4)	C(11)–C(12)	1.391(6)
Fe–C(4)	2.033(4)	C(12)–C(13)	1.367(6)
Fe–C(5)	2.032(4)	C(13)–C(14)	1.371(5)
Fe–C(6)	2.038(4)	C(14)–C(15)	1.396(5)
Fe–C(7)	2.048(4)	C(15)–C(16)	1.384(5)
Fe–C(8)	2.044(4)	C(16)–C(11)	1.398(5)
Fe–C(9)	2.038(4)	C(1)–C(17)	1.484(5)
Fe–C(10)	2.033(4)	C(17)–C(18)	1.340(4)
C(1)–C(2)	1.434(5)	C(18)–C(19)	1.480(5)
C(2)–C(3)	1.415(6)	C(19)–C(20)	1.382(6)
C(3)–C(4)	1.413(6)	C(20)–C(21)	1.391(6)
C(4)–C(5)	1.415(6)	C(21)–C(22)	1.370(6)
C(5)–C(1)	1.422(5)	C(22)–C(23)	1.370(7)
C(6)–C(7)	1.406(6)	C(23)–C(24)	1.390(5)
C(7)–C(8)	1.402(6)	C(24)–C(19)	1.392(5)
C(8)–C(9)	1.410(6)	C(16)–C(17)	1.497(5)

diffraction. The molecular geometry (Figure 1) shows that the (*Z*)-stereochemical assignment is correct. There is nothing unusual in the bond-length and bond-angle values (Tables 3 and 4). Both ferrocenyl rings are accurately planar, tilted by 1.05°, with a mean Fe–C bond length of 2.036(4) Å; the ferrocenyl rings are arranged in an almost eclipsed configuration.[7] The C(17)–C(18) bond length (1.340 Å) is consistent with a carbon–carbon double bond. The angles about C(17) are reasonably trigonal but those about C(18) show appreciable deviation from 120°, a distortion which was not influenced by the C(18)–H(15) calculation. The arrangement about the double bond is by no means planar (Table 5) with a dihedral angle of 8.6° between the C(1),C(16),C(17) and C(18),C(19),H(15) planes. The planes of the C(1)—C(5) cyclopentadienyl ring and the C(11)—C(16) and C(19)—C(24) phenyl rings are twisted by *ca.* ±45° from the double-bond plane, indicating minimal π conjugation through the *trans*-stilbene and *cis*-styrylferrocene moieties.

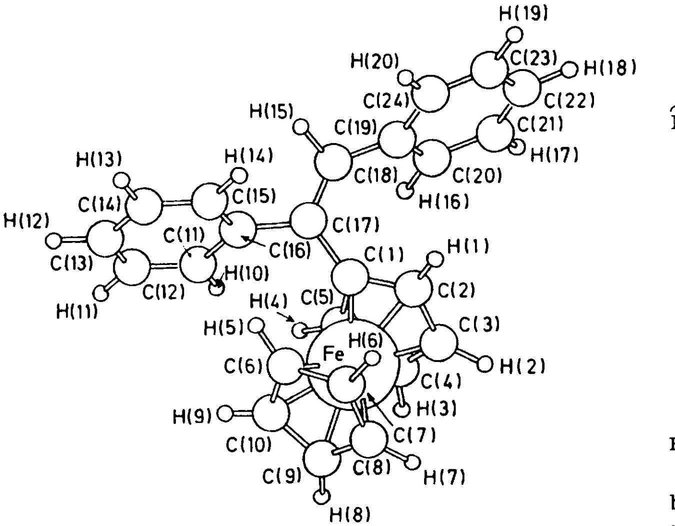

FIGURE 1 A perspective drawing of the title molecule, showing the atom-numbering scheme

To our knowledge, the crystal structure of only one other 1-alkenylferrocene, *viz.* 1-(2,2-dicyanoethenyl)-ferrocene, has been reported [8] previously. In this case, steric repulsion between the ferrocenyl C_5H_4 ring and the *cis* group (CN) is less severe than for (3e) and the double-bond plane is twisted by only 13° from the plane of the adjacent ring.

TABLE 4

Bond angles (°)

C(1)–C(2)–C(3)	108.8(3)	C(11)–C(12)–C(13)	121.3(4)
C(2)–C(1)–C(5)	106.3(3)	C(12)–C(13)–C(14)	119.5(4)
C(2)–C(3)–C(4)	107.8(4)	C(13)–C(14)–C(15)	120.2(4)
C(3)–C(4)–C(5)	108.2(4)	C(14)–C(15)–C(16)	120.8(3)
C(1)–C(5)–C(4)	108.9(3)	C(11)–C(16)–C(15)	118.3(3)
C(6)–C(7)–C(8)	108.1(3)	C(11)–C(16)–C(17)	121.8(3)
C(7)–C(8)–C(9)	108.2(4)	C(15)–C(16)–C(17)	119.9(3)
C(8)–C(9)–C(10)	108.2(4)	C(17)–C(18)–C(19)	128.4(3)
C(9)–C(10)–C(6)	107.5(4)	C(18)–C(19)–C(20)	122.1(3)
C(7)–C(6)–C(10)	108.0(3)	C(18)–C(19)–C(24)	119.1(3)
C(5)–C(1)–C(17)	130.6(3)	C(20)–C(19)–C(24)	118.6(3)
C(2)–C(1)–C(17)	123.0(3)	C(19)–C(20)–C(21)	120.8(4)
C(1)–C(17)–C(16)	120.8(3)	C(20)–C(21)–C(22)	119.8(4)
C(1)–C(17)–C(18)	121.4(3)	C(21)–C(22)–C(23)	120.3(4)
C(16)–C(17)–C(18)	117.7(3)	C(22)–C(23)–C(24)	120.2(4)
C(12)–C(11)–C(16)	119.8(4)	C(19)–C(24)–C(23)	119.9(5)

TABLE 5

Dihedral angles between mean planes *

Planes		Dihedral angle (°)					
No.	Atoms	1	2	3	4	5	6
1	C(1)—C(5)						
2	C(6)—C(10)	1.05					
3	C(11)—C(16)	38.51	37.66				
4	C(19)—C(24)	125.29	126.02	162.27			
5	C(1), C(16)—C(19), H(15)	131.69	131.46	134.52	44.34		
6	C(1), C(16), C(17)	132.12	131.81	132.08	47.54	3.39	
7	C(18), C(19), H(15)	130.00	129.83	137.48	39.80	5.21	8.59

* The equations of the mean planes and deviations therefrom have been deposited.

EXPERIMENTAL

The methods of preparation of the alkenes studied have been described previously.[1,2,9] Stereoisomeric alkenes were separated by preparative t.l.c. on plates coated with Merck Kieselgel G type 60, using light petroleum as eluant. Hydrogen-1 n.m.r. spectra were recorded at 60 and 90 MHz using Perkin-Elmer spectrometers, and electronic spectra were obtained using a Unicam SP 800A spectrometer.

Crystal Data.—Crystals of (3e) were grown from light petroleum (b.p. 40—60 °C). $C_{24}H_{20}Fe$, $M = 364.08$, Monoclinic, $a = 17.603(2)$, $b = 10.218(2)$, $c = 10.072(2)$ Å, $\beta = 103.27(2)°$, $U = 1\,763.27$ Å^3, $D_m = 1.30$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.369$ g cm^{-3}, $F(000) = 759.96$, $\lambda = 0.709\,26$ Å and $\mu = 8.01$ cm^{-1} (for Mo-K_α radiation), space group $P2_1/c$ (C_{2h} no. 14) from systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$.

Structure Elucidation.—The data were collected and the unit-cell data were refined on a Hilger and Watts four-circle diffractometer. A needle-shaped crystal of dimensions *ca.* 0.4 × 0.3 × 0.1 mm was used, mounted along the unique axis; 2 219 independent reflections with $I > 3\sigma(I)$ in the range $0 \leqslant 2\theta \leqslant 22°$ were considered observed and were used in the subsequent refinement. No account was taken of anomalous dispersion and no corrections were made for secondary extinction or absorption effects; the maximum error introduced by neglect of absorption effects was estimated to be *ca.* 15% in F^2.

Data reduction was carried out on the ICL 1906A computer at Nottingham University, and subsequent crystallographic calculation on the IBM 370/138 computer at University College, Cork, using the SHELX 76, XANADU, PLUTO, and XPUB programs of Drs. G. Sheldrick and S. Motherwell (University of Cambridge). Literature values[10] for the atomic-scattering factors were used. The position of the metal atom was located from a three-dimensional Patterson synthesis, and subsequent Fourier synthesis phased on the heavy-atom position indicated the positions of all the carbon atoms. The atom positions and their anisotropic thermal parameters were then refined using least-squares procedures, in which $\Sigma w|F_o - F_c|^2$ was the function minimised. Calculated hydrogen positions were used, with a fixed C–H bond length of 1.08 Å (including a fixed temperature factor of 0.07 Å), and floated on the associated carbon atom; in order to perform this calculation for the cyclopentadienyl rings, the iron atom had to be removed and replaced before further least-squares refinement. A refined weighting scheme was used, where $w = k/[\sigma^2(F_o) + g(F_o)^2]$, and yielded final values of $R = 0.043$ and $R' = 0.046$ with $k = 1.638$ and $g = 0.000\ 725$, where $R = (\Sigma\Delta/\Sigma|F_o|)$ and $R' = (\Sigma\Delta w^2/\Sigma|F_o|w^{\frac{1}{2}})$. The final shift/least-squares deviation was <0.031 and the maximum residual electron density was 0.44 e Å^{-3}.

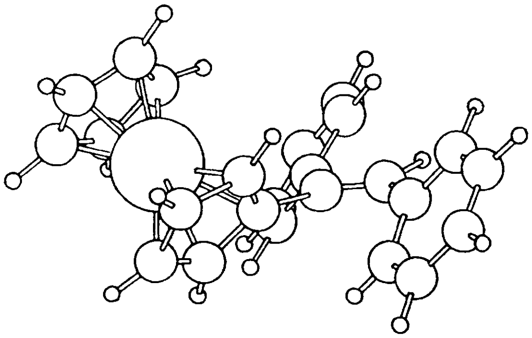

FIGURE 2 A view of the title molecule showing the twisting of ferrocenyl and phenyl groups from the double-bond plane

The final atomic co-ordinates are in Table 6. Thermal parameters, calculated hydrogen atom positions, lists of structure factors, and equations of some relevant mean planes are available as Supplementary Publication No. SUP 22482 (18 pp.).* Figures 1 and 2 illustrate two projections of the molecular geometry and the atom numbering scheme used is shown in the former.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 6

Atom co-ordinates ($\times 10^4$)

	x/a	*y/b*	*z/c*
Fe	1 159	494(1)	3 355(1)
C(1)	2 234(2)	−386(3)	3 770(3)
C(2)	2 079(2)	217(4)	4 966(3)
C(3)	1 397(2)	−351(4)	5 239(4)
C(4)	1 119(3)	−1 296(4)	4 219(4)
C(5)	1 630(2)	−1 317(3)	3 320(4)
C(6)	1 157(2)	1 964(4)	1 987(4)
C(7)	943(2)	2 462(4)	3 151(4)
C(8)	272(2)	1 798(4)	3 305(4)
C(9)	64(2)	887(5)	2 231(4)
C(10)	611(2)	981(5)	1 414(4)
C(11)	2 422(2)	−631(4)	730(4)
C(12)	2 395(3)	−391(4)	−639(4)
C(13)	2 767(3)	665(4)	−1 034(4)
C(14)	3 160(3)	1 518(4)	−66(4)
C(15)	3 195(2)	1 296(4)	1 314(4)
C(16)	2 836(2)	214(3)	1 730(3)
C(17)	2 923(2)	−50(3)	3 219(3)
C(18)	3 636(2)	75(3)	4 037(4)
C(19)	3 893(2)	−249(4)	5 504(4)
C(20)	3 663(2)	−1 386(4)	6 045(4)
C(21)	3 950(3)	−1 701(5)	7 412(4)
C(22)	4 469(3)	−880(5)	8 235(4)
C(23)	4 709(3)	247(5)	7 717(4)
C(24)	4 432(2)	562(4)	6 349(4)

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