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X-ray diffraction studies of mesomorphic ferrocene diesters

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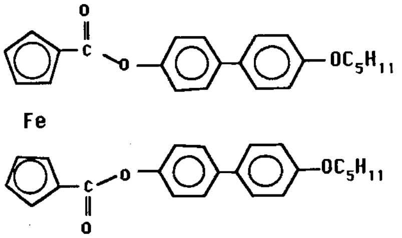
The crystal and molecular structure of 1,1′-bis(4′-pentyloxybiphenyl)ferrocene dicarboxylate ester (**1**) has been determined by X-ray diffraction at 295 and 160 K. The molecule is found to exist at both temperatures in an extended S geometry. The carboxyl groups are essentially coplanar with the cyclopentadienyl rings but almost perpendicular to the attached phenyl ring. Low angle X-ray diffraction of three diesters in the smectic phases were also studied. The results were not very definitive because of the lack of thermal stability for the monotropic phase behaviour. Nevertheless, the layer spacing of about 47 Å for one of the compounds at 409 K is consistent with the extended S shape conformation.

1. Introduction

In recent years there has been considerable interest in liquid crystals that contain transition metals, because of their potentially unusual electronic, magnetic and chromatic properties [1–4]. The first liquid crystal prepared containing a transition metal was a ferrocene ester [5]. The ferrocene moiety in the compound, however, is an appendage to a mesogenic unit rather than being in the core of the molecule. We have recently synthesized a series of ferrocene diesters which have the ferrocene moiety at the centre of the molecule [6]. Three of the compounds in this homologous series exhibit mesomorphic properties. All of them are monotropic; two have a smectic C phase and the other has a smectic A phase [6].

The most likely conformation of these liquid crystals is either a U shape as shown in structure **1** or an S shape with the two alkyl chains extending in opposite directions. We have determined the crystal structure of **1** ($R = C_5H_{11}$) at 160 and 295 K and carried out low angle X-ray diffraction studies of **1** and its homologues which exhibit monotropic smectic phases, in an attempt to measure the layer thickness. The results are presented.



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X-ray investigations of mesogenic molecules can provide very important information regarding the conformation of the molecule and the molecular packing. The crystal and molecular structures of the commonly encountered liquid crystals such as the alkyl-cyanobiphenyls [7, 8], alkyl-cyanophenylcyclohexanes [9], alkyl-cyanocyclohexylcyclohexanes [10] and substituted biphenylcyclohexanes [11] have been determined. Since compound **1** and two of its homologues are the first known mesogenic compounds with the ferrocene moiety at the centre of the molecule, the X-ray study can provide valuable information regarding the molecular structure and the conformation of the ferrocene diesters in the smectic phases.

2. Experimental

Crystals suitable for X-ray analysis were grown in a mixture of *n*-hexane and benzene. The crystal selected was mounted on a glass fibre and the data were collected in an Enraf–Nonius CAD-4 automatic X-ray diffractometer fitted with a liquid nitrogen low temperature device, using Mo-K_α radiation (λ = 0·710 69 Å) by the methods that are standard in this laboratory [12]. Unit cell dimensions were obtained by least-squares analysis of the diffractometer angular setting of 25 well centred reflections ($2q$ range = 30–40°). The data were corrected for Lorentz and polarization effects; no absorption correction was applied since it was deemed to be negligible. The atomic scattering factors were obtained from [13]. The structure was solved by the heavy atom method and refined by least-squares (SHELX-76) [14] minimizing $\Sigma w(|F_0| - |F_c|)^2$. All of the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were refined isotropically. Data regarding collection and refinement are summarized in table 1. Tables comprising 17 pages containing information on atomic coordinates, bond lengths and angles, and thermal parameters are deposited in the British Library Document Supply Centre, copies of this Supplementary

Table 1. Crystal data for **1**.

Molecular formula	$C_{46}H_{46}O_6Fe$	
Molecular weight/g mol^{-1}	749·85	
Crystal size/mm	0·2 × 0·3 × 0·3	
Radiation (monochromated) λ (Mo-K_α)	0·710 69 Å	
System	Triclinic	
Space group	$P\bar{1}$	
Temperature for data collection/K	295 ± 2	160 ± 2
Cell dimensions:		
a/Å	8·697[3]	8·492[4]
b/Å	10·359[4]	10·295[5]
c/Å	10·898[4]	10·843[5]
α/°	76·35[2]	77·09[3]
β/°	87·21[3]	88·58[3]
γ/°	80·81[3]	81·04[3]
Volume/Å^3	941·8	912·7
Z	1	1
Density (calc.)/g cm^{-3}	1·322	1·364
Data collection range	$3° < 2\theta < 53°$	$3 < 2\theta < 53°$
Total reflections measured	3863 ($\pm h$, $\pm k$, l)	3780 ($\pm h$, k, l)
Reflections used [$I > 2\sigma(I)$]	2389	2987
$R = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0·033	0·039
$Rw = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma w F_0^2]^{1/2}$	0·039	0·048
ϱ_{max} in the final diff. map/e Å^{-3}	0·3	0·5

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The specimens for the X-ray diffraction studies in the liquid-crystalline phase (409 K) were prepared in the following way. A very small amount of crystalline powder was introduced into a 1·5 mm diameter quartz X-ray capillary tube. The capillary was then flushed with argon gas and immediately sealed. The specimen was placed in a furnace consisting of a resistance-wire wound copper cylinder jacketed with Teflon. The triac based temperature controller gave temperature stability of ± 0·5 K. Temperatures were measured using a copper–constantan thermocouple. For the compound with the hexyl chain, the sample was incubated at 473 K for 2–3 h and then cooled to 409 K, where the data were recorded. The X-ray measurements were made using a Searle camera equipped with Franks optics and affixed to one port of an Elliot GX6 rotating anode generator operating at approximately 1·5 kW. The generator produces copper radiation (λ_{av} = 1·54 Å) which is focussed by a 200 μm focal cap and nickel filtered. Diffraction patterns were registered on direct exposure film (Kodak) for approximately 16 h.

3. Results and discussion

The structure of 1,1′-bis(4′-pentyloxybiphenyl)ferrocene dicarboxylate ester (**1**) was determined at two different temperatures, 295 and 160 K. At both of these temperatures the structure is essentially the same with an approximately 50 per cent reduction of thermal motion at the lower temperature as indicated from the U(Eq) values.

The structure of the molecule with the atom numbering scheme is shown in figure 1. The bond lengths and angles, as given in the Supplementary Publication, are unexceptional. The interesting feature of the two structures is the dihedral angles between different planes. The planes are defined as follows: $C_{(1)}$–$C_{(5)}$, Plane 1; $C_{(1)}$, $C_{(6)}$, $O_{(1)}$, $O_{(2)}$, Plane 2; $C_{(7)}$–$C_{(12)}$, Plane 3; $C_{(13)}$–$C_{(18)}$, Plane 4. The dihedral angles are listed in table 2. The data in this table indicate that the carboxyl group is essentially coplanar with the cyclopentadienyl ring, but is almost perpendicular to the first phenyl ring. The dihedral angle between the two phenyl rings is about 23(1)°, which is considerably smaller than the value of 42·8° for 3CB (4-*n*-propyl-4′-cyanobiphenyl [7]. The small torsional angle indicates that the $C_{(19)}$ and $C_{(20)}$ in the pentyloxy chain are essentially coplanar with the phenoxy group.

The crystal packing of **1** is shown in figure 2. The crystals consist of discrete molecules separated by van der Waals distances. The shortest intermolecular contact

Table 2. Dihedral angles between planes in **1**.

Planes	Angle between planes/° at 295 K	Angle between planes/° at 160 K
1, 2	4·5(7)	4·9(5)
1, 3	99·4(1)	96·8(1)
1, 4	122·0(1)	119·7(1)
3, 4	22·7(2)	23·1(2)
Torsional angle $C_{(17)}$–$C_{(16)}$–$O_{(3)}$–$C_{(19)}$	0·9(3)	0·2(3)

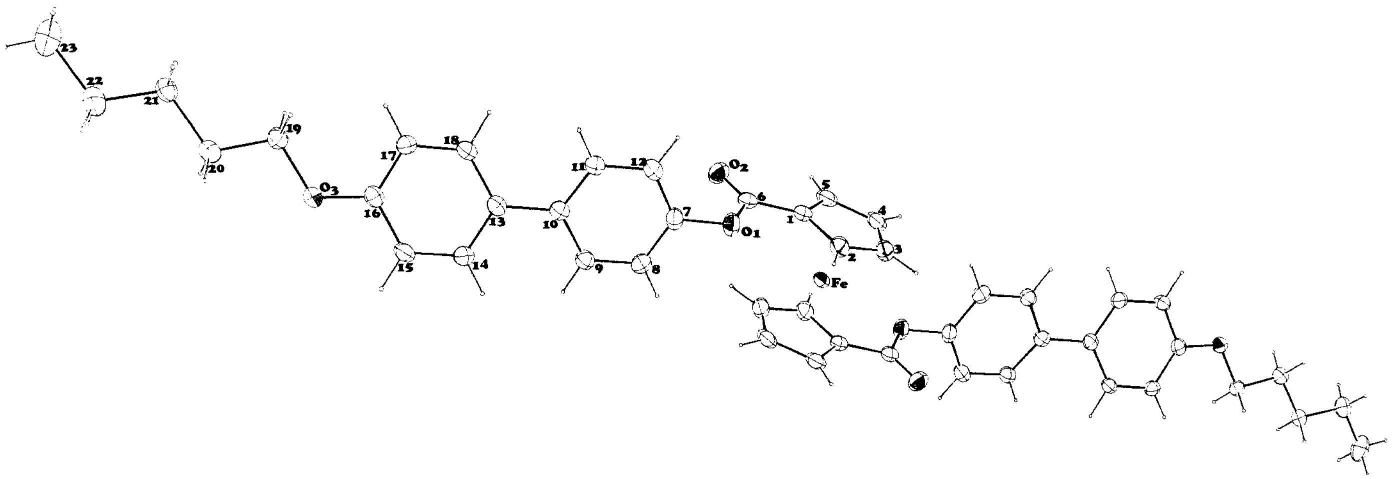

Figure 1. X-ray structure of **1**.

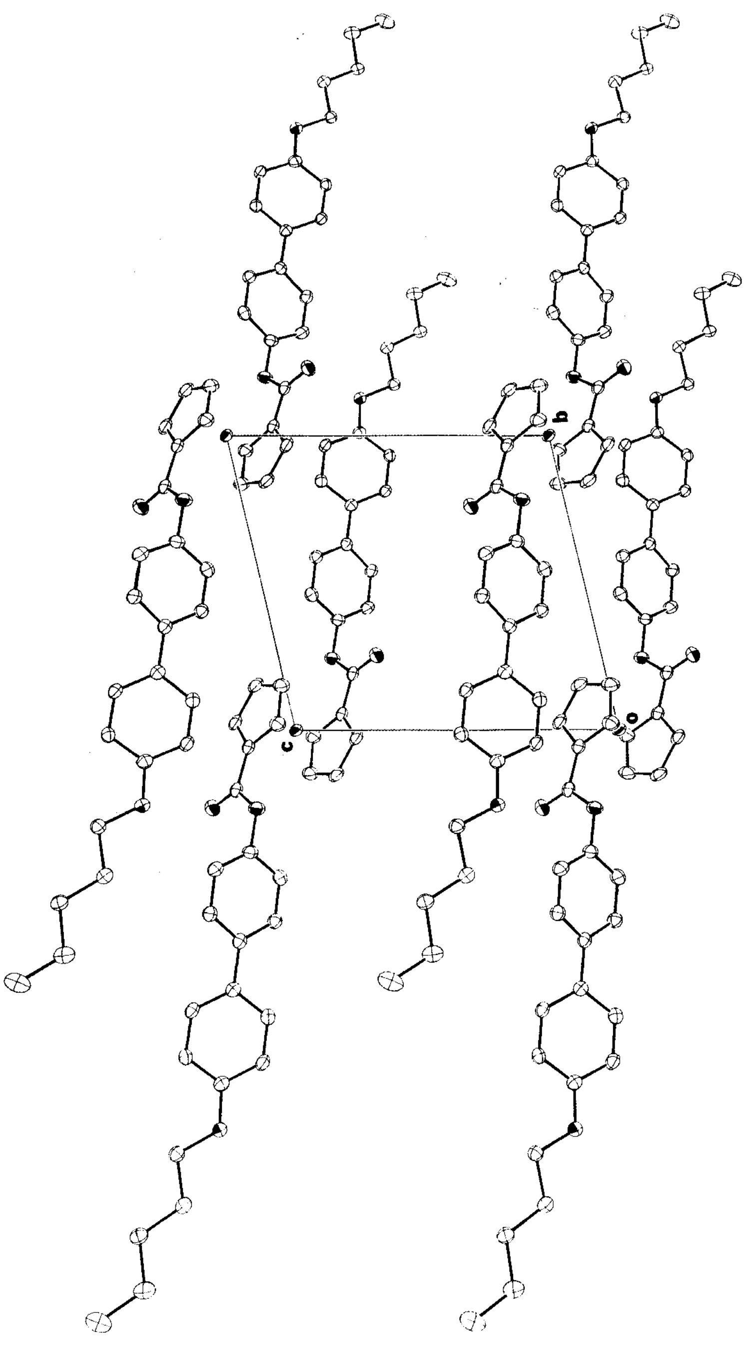

Figure 2. Packing diagram projected along the **a** axis for 1.

between two non-hydrogen atoms is between $C_{(2)}$ and $C_{(15)}$, and the values are 3·662(4) and 3·601(4) Å at 295 ± 2 and 160 ± 2 K, respectively.

For the X-ray study in the liquid-crystalline phase, one of the films of the compound with a hexyl chain showed what we believe to be an evidence for a mixture of mesophase and crystalline solid at 409 K. The reflections from the crystalline solid were confined to angles characteristic of spacings 18 Å and smaller "spotty" rings. At small angles, a set of reflections which could be indexed as the first three orders of a layer spacing of approximately 47 Å were observed (the specimen–film distance was calibrated using auxiliary electronic detector measurements). These reflections were well oriented in a plane almost normal to the axis of the capillary tube.

In the smectic phases it is likely that the phenyl rings undergo rapid rotation or jumps between equilibrium positions. The alkyl tails would also have large thermal vibrations and various internal rotations between the C–C bonds. Although the two cyclopentadienyl rings in ferrocene itself undergo rapid rotations about the C_5 axis [15–19], the large substituents would prevent them from doing so in the smectic phases. Even though the low-angle X-ray diffraction results in the smectic phases of the ferrocene diesters are not extremely definitive because of the lack of thermal stability of the monotropic phase behaviour, the approximate layer spacing of 47 Å is consistent with an extended conformation. Therefore, we suggest that the conformation of **1** in the smectic C phase is an S shape like that in the solid (see figures 1 and 2) rather than a U shape as depicted in the simplified molecular structure shown in §1.

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