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Keto-acid chloride and diketone intermediates in the acylation of ferrocene by arylene bis-acid chlorides. Crystal and molecular structure of 4-ferrocenylcarbonyl-4′-chlorocarbonylbiphenyl: intermolecular association by means of strong C–H···O hydrogen bonds and π···π stacking interactions

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Abstract

Acylation of ferrocene with arylene bis-acid chlorides yields deep-red polymeric products. However, under controlled conditions two types of intermediate can be isolated and characterised: the keto-acid chlorides FcCO(arylene)COCl **1** [Fc = $(C_5H_5)Fe(C_5H_4)$; **a** arylene = 4,4′-$C_6H_4C_6H_4$, **b** arylene = 1,3-C_6H_4, **c** arylene = 1,4-C_6H_4], followed in the case of **1a** and **1b** by the diketones FcCO(arylene)COFc **2a** and **2b**, although no conversion of **1c** to **2c** occurs. Similarly, use of 1,3,5-benzenetricarbonyl trichloride yielded 1,3,5-$C_6H_3(COFc)_3$. In the crystal structure of **1a**, there are four independent molecules: pairs of molecules are linked into dimers by strong C–H···O hydrogen bonds, and these dimers are linked into chains by π···π stacking interactions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene derivatives; Acylation by arylene bis-acid chlorides; Intermolecular H-bonding; π–π Stacking

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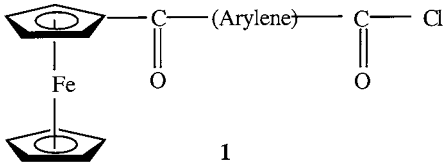
1. Introduction

In Friedel–Crafts acylation of ferrocene, the deactivating effect of a newly introduced acyl substituent leads to (a) a large difference in rates between the first and second acylation steps, so that monoacyl products are readily isolable and (b) exclusively hetero-annular diacylation [1]. When bis-acid chlorides are employed in the acylating agent, the formation of linear polyketone polymers is thus to be expected, while tris-acid chlorides should lead to dendrimeric polymers. One advantage of polymer synthesis using acylation methods is that ferrocene-containing polyketone polymers can be produced from ferrocene itself in a single-step process: this contrasts with most other types of ferrocene-containing polymers, whose syntheses from ferrocene generally require several steps [2–5].

In seeking methods for the controlled growth of such polymers, we have now investigated the early steps in the acylation of ferrocene with some simple arylene bis-acid chlorides, and here we report the isolation and characterisation of some of the early intermediates **1** and **2**, including the single-crystal X-ray structure of **1a**. The structure of **1a** exhibits supramolecular association employing a combination of strong C–H···O hydrogen bonds and aromatic π···π stacking interactions.



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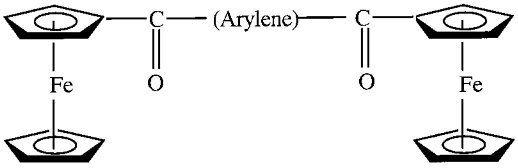

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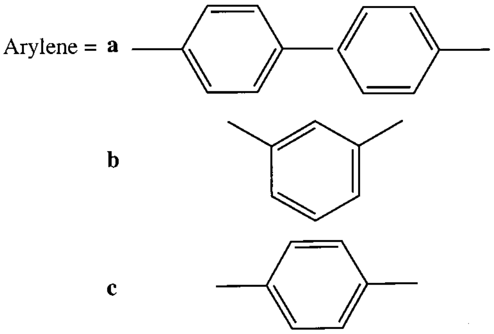


2. Experimental

2.1. Synthesis

2.1.1. Acylation reactions using arylene bis(carbonyl chlorides): general procedures

Stoichiometric quantities of ferrocene dissolved in dry CH_2Cl_2 were added to a well-stirred solution containing the acid chloride and anhydrous $AlCl_3$. This mixture was then stirred either at 0°C or at reflux temperature for the required time. Work-up consisted of quenching the reaction with ice/water, filtration or extraction of the organic material with CH_2Cl_2, washing of the organic material until neutral. For soluble products, the extract was then dried, concentrated and chromatographed on silica. Three variants were employed: in procedure A, one equivalent of ferrocene per mole of acid chloride was employed, and the reaction mixture was refluxed for 8 h, producing copious quantities of a deep-red solid, isolated by filtration; in procedure B, two equivalents of ferrocene were employed, and reactions were refluxed for 8–10 h; in procedure C, one equivalent of ferrocene was used, the reaction was run at 0°C and its progress was monitored by TLC until the abundance of the first intermediate was judged to be at a maximum, when the reaction was quenched.

2.1.2. Reactions with 4,4′-bis(chlorocarbonyl)biphenyl

Procedure A produced a deep-red powder, isolated by filtration, whose ^{1}H-NMR spectrum showed resonances characteristic of C_5H_5, C_5H_4 and 4,4′-biphenylyl groups in the approximate ratio 1:3:3. In procedure B chromatography provided, upon elution with 10% petrol in CH_2Cl_2, 4,4′-bis(ferrocenecarbonyl)biphenyl **2a** in 80% yield. Anal. Calc. for $C_{34}H_{26}Fe_2O_2$: C, 70.5; H, 4.5. Found: C, 70.5; H, 4.4%. NMR δ(H) 4.27 (s, 10H, 2 × C_5H_5), 4.62 (m, 4H) and 4.97 (m, 4H) (2 × C_5H_4), 7.76 and 8.04 (8H, AB, 2 × C_6H_4): δ(C) 70.3 (d, C_5H_5), 71.5 (d), 72.7 (d) and 78.2 (s) (C_5H_4), 127.1 (d), 128.8 (d), 139.1 (s) and 143.2 (s) (C_6H_4), 198.5 (s, CO). IR (Nujol) ν(CO) 1645 cm^{-1}. Procedure C gave, using similar elution conditions, 4′-chlorocarbonyl-4-biphenyl ferrocenyl ketone (**1a**) in 30% yield. Anal. Calc. for $C_{24}H_{17}ClFeO_2$: C, 67.2; H, 4.0. Found: C, 67.3; H, 3.8%. NMR δ(H) 4.26 (s, 5H, C_5H_5), 4.67 (m, 2H) and 4.98 (m, 2H) (C_5H_4), 7.75 and 8.05 (4H, AB), 7.82 and 8.28 (4H, AB) (2 × C_6H_4): δ(C) 70.4 (d, C_5H_5), 71.6 (d), 72.9 (d) and 78.1 (s) (C_5H_4), 127.3 (d), 128.9 (d), 139.8 (s) and 142.0 (s) (C_6H_4COFc), 127.7 (d), 132.1 (d), 132.4 (s) and 147.0 (s) (C_6H_4COCl), 168.0 (s, COCl), 198.1 (s, COFc). IR (Nujol) ν(CO) 1755 cm^{-1}.

2.1.3. Reactions with isophthaloyl dichloride

Procedure A produced a deep-red powder, isolated by filtration, whose ^{1}H-NMR spectrum showed resonances characteristic of C_5H_5, C_5H_4 and 1,3-biphenylene groups in the approximate ratio 1:20:20. In procedure B, chromatographic elution with CH_2Cl_2 provided an 83% yield of 1,3-bis(ferrocenecarbonyl)benzene (**2b**) in 83% yield. Anal. Calc. for $C_{28}H_{22}Fe_2O_2$: C, 67.0; H, 4.4. Found: C, 66.8; H, 4.5%. NMR δ(H) 4.26 (s, 10H, 2 × C_5H_5), 4.65 (m, 4H) and 4.95 (m, 4H) (2 × C_5H_4), 7.58 (t, $J = 12$ Hz, 1H), 8.10 (d, $J = 12$ Hz, 2H) and 8.58 (s, 1H) (C_6H_4): δ(C) 70.3 (d, C_5H_5), 71.5 (d), 72.8 (d) and 77.7 (s) (C_5H_4), 128.0 (d), 128.4 (d), 130.9 (d) and 139.5 (s) (C_6H_4), 198.5 (s, CO). IR (Nujol) ν(CO) 1640 cm^{-1}. Using similar elution conditions, procedure C gave a very small quantity of (3-chlorocarbonylphenyl) ferrocenyl ketone (**1b**) (yield < 10%). NMR δ(H) 4.30 (s, 5H, C_5H_5), 4.70 (m, 2H) and 4.90 (m, 2H) (C_5H_4), 7.66 (m, 1H), 8.18 (d, 1H0, 8.32 (d, 1H0 and 8.84 (s, 1H) (C_6H_4): δ(C) 70.8 (d, C_5H_5), 71.5 (d), 73.2 (d) and 77.4 (s) (C_5H_4), 129.4 (d), 130.9 (d), 133.2 (s), 133.9 (d), 134.7 (d) and 140.4 (s) (C_6H_4), 168.0 (s, COCl), 198.1 (s, COFc). IR (Nujol) ν(CO) 1770 cm^{-1}.

2.1.4. Reactions with terephthaloyl dichloride

Procedure B with 24 h reflux, provided (4-chlorocarbonylphenyl) ferrocenyl ketone (**1c**) in 20% yield. NMR δ(H) 4.25 (s, 5H, C_5H_5), 4.68 (m, 2H) and 4.90 (m, 2H) (C_5H_4), 7.98 and 8.24 (4H, AB, C_6H_4): δ(C) 70.4 (d, C_5H_5), 71.4 (d), 73.4 (d) and 77.2 (s) (C_5H_4), 128.2 (d), 131.3 (d), 135.1 (s) and 145.4 (s) (C_6H_4), 167.9 (s, COCl), 198.1 (s, COFc). IR (Nujol) ν(CO) 1765 cm^{-1}.

2.1.5. Acylation of ferrocene using 1,3,5-benzenetricarbonyl trichloride

A mixture of 1,3,5-benzenetricarbonyl trichloride (0.66 g, 2.5 mmol), anhydrous $AlCl_3$ (2.0 g, 15 mmol) and ferrocene (1.67 g, 9 mmol) in dry CH_2Cl_2 (100 cm^3) was refluxed for 16 h. The mixture was worked up as

Table 1
Experimental details for **1a**

Crystal data	
Chemical formula	$C_{24}H_{17}ClFeO_2$
Chemical formula weight	428.68
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	14.8547(9)
b (Å)	18.3258(17)
c (Å)	24.757(2)
α (°)	90
β (°)	97.043(6)
γ (°)	90
V (Å^3)	7769.4(11)
Z	16
D_{calc} (Mg m^{-3})	1.466
Radiation type	Mo–K$_\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	25
θ Range for cell measurement (°)	8.90–14.29
μ (mm^{-1})	0.931
Temperature (K)	294(1)
Crystal form	Plate
Crystal size (mm)	$0.38 \times 0.35 \times 0.04$
Crystal colour	Orange
Data collection	
Diffractometer	Enraf–Nonius CAD4
Data collection method	$\theta/2\theta$ Scans
Absorption correction	Gaussian
No. of measured reflections	12 534
No. of independent reflections	12 232
No. of observed reflections	4011
Criterion for observed reflections	$[I>2\sigma(I)]$
R_{int}	0.015
θ_{max} (°)	25.12
Index ranges	$-17<h<17$, $0<k<21$, $-34<l<27$
No. of standard reflections	3
Frequency of standard reflections (min)	120
Intensity decay (%)	2.0
Refinement	
Refinement on	F^2
$R[F^2>2\sigma(F^2)]$	0.0464
$wR(F^2)$	0.1349
S	0.835
No. of reflections used in refinement	12 232
No. of parameters used	863
No. of restraints	1780
H-atom treatment	Riding
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0582P)^2]$, where $P=(F_o^2+2F_c^2)/3$
(Δ/σ) max.	0.003
$\Delta\rho_{max}$ (e Å^{-3})	0.280
$\Delta\rho_{min}$ (e Å^{-3})	−0.262
Source of atomic scattering factors	International Tables for Crystallography (vol. C)
Computer programs	
Data collection	CAD4-PC Software [6]
Cell refinement	SET4 and CELDIM in CAD4-PC Software [6]
Data reduction	DATRD2 in NRCVAX-96 [7]
Structure solution	SOLVER in NRCVAX-96
Structure refinement	NRCVAX-96 and SHELXL-97 [9]
Graphics	PLATON [8]
Preparation of material for publication	NRCVAX-96, SHELXL-97 and WordPerfect macro PREP-8 [10]

usual and chromatographed on silica, when CH_2Cl_2 eluted unreacted ferrocene (1.1 g, 5.9 mmol) and 1,3,5-tris(ferrocenecarbonyl)benzene (0.5 g, 23% based on ferrocene consumed). NMR δ(H) 4.30 (s, 15H, $3 \times C_5H_5$), 4.70 (m, 6H) and 4.95 (m, 6H) ($3 \times C_5H_4$), 8.78 (s, 3H, C_6H_3): δ(C) 71.2 (d, C_5H_5), 72.2 (d), 73.8 (d) and 778.7 (s) (C_5H_4), 131.7 (d) and 140.4 (s) (C_6H_3), 198.3 (s, CO). IR (Nujol) ν(CO) 1645 cm^{-1}.

2.2. X-ray crystallography

Crystals of **1a** suitable for single-crystal X-ray diffraction were grown form CH_2Cl_2 solution. Details of the crystal data, diffraction data collection, and structure solution and refinement [6–10] are given in Table 1: the 2% intensity decay during data collection was allowed for by linear scaling.

The systematic absences permitted two possible space groups, *Cc* and *C*2/*c*. The unit cell dimensions, together with an estimated density of ca. 1.4–1.5 g cm^{-3} typical of the densities found in other acyl ferrocenes, indicated $Z=16$, i.e. $Z'=4$ [11] for *Cc* or $Z'=2$ for *C*2/*c*. However, attempts to solve the structure, either by direct methods or by Patterson methods, were uniformly unsuccessful in both of the possible space groups. Careful inspection of the intensity statistics had already shown that the population of the parity groups *eee* and *eeo* was far higher than that of the groups *ooe* and *ooo*, while the other four groups were systematically absent. This intensity distribution suggested an alternative approach to the structure solution.

Use of only the *eee* and *eeo* data, and conversion to a quarter sized unit cell ($\mathbf{a} \rightarrow \mathbf{a}/2$, $\mathbf{b} \rightarrow \mathbf{b}/2$, $\mathbf{c} \rightarrow \mathbf{c}$) with an appropriate origin shift allowed a straightforward Patterson solution in $P2_1/c$ with $Z'=1$. Development of this solution revealed all the carbon atoms of the ferrocenyl fragment with full occupancy, and two $COC_6H_4C_6H_4COCl$ fragments, one bonded to each cyclopentadienyl ring and each having site occupation factor 0.5. Refinement of this disordered $P2_1/c$ solution using only the *eee* and *eeo* groups of the original data, suitably transformed, converged at $R=0.05$.

Conversion of the $P2_1/c$ solution back to the original cell and testing the various possibilities for the location

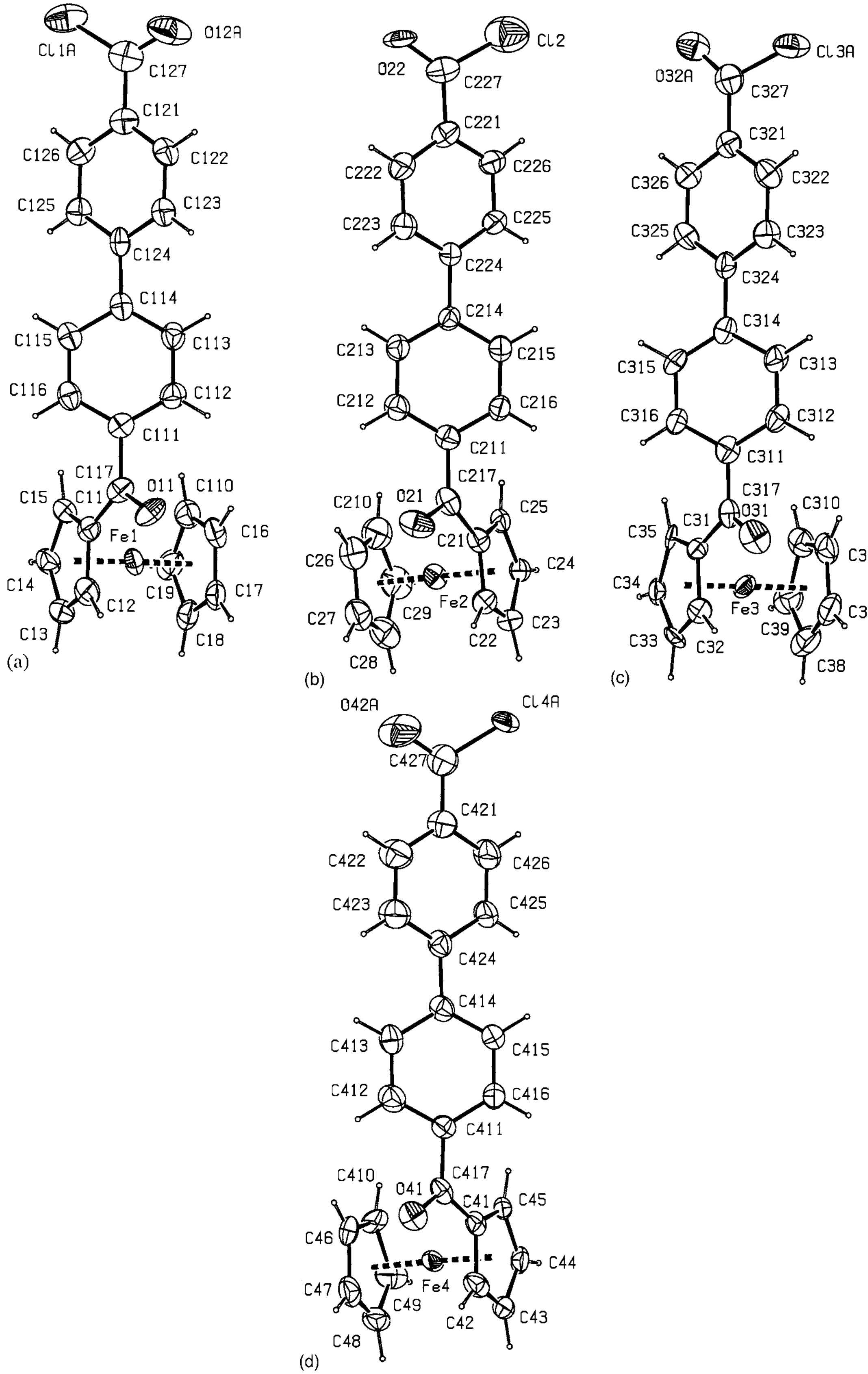


Fig. 1. Views of the four independent molecules in the crystal structure of **1a**, showing the atom-labelling scheme and the rotational disorder of the chlorocarbonyl groups in molecules 1, 3 and 4. Displacement ellipsoids are drawn at the 30% probability level.

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1a**

Atom	x	y	z	U_{eq} [a]
Fe1	0.39476(17)	0.07787(14)	0.28922(8)	0.0511(8)
C11	0.3482(7)	0.0268(6)	0.3441(3)	0.053(3)
C12	0.3738(7)	−0.0263(5)	0.3122(4)	0.069(4)
C13	0.3227(8)	−0.0134(6)	0.2679(3)	0.069(4)
C14	0.2656(7)	0.0477(6)	0.2724(3)	0.062(4)
C15	0.2814(7)	0.0725(5)	0.3195(4)	0.060(4)
C16	0.4995(7)	0.1408(7)	0.3130(3)	0.071(4)
C17	0.5274(7)	0.0895(6)	0.2806(4)	0.065(3)
C18	0.4731(7)	0.1001(6)	0.2370(3)	0.067(4)
C19	0.4116(7)	0.1579(7)	0.2424(4)	0.076(4)
C110	0.4279(7)	0.1831(6)	0.2894(4)	0.074(4)
C111	0.3624(7)	0.1016(4)	0.4221(2)	0.052(3)
C112	0.4263(5)	0.1457(5)	0.4478(3)	0.064(3)
C113	0.3991(5)	0.1965(4)	0.4791(3)	0.061(3)
C114	0.3079(6)	0.2031(4)	0.4848(2)	0.052(3)
C115	0.2439(4)	0.1590(4)	0.4591(3)	0.055(3)
C116	0.2711(6)	0.1082(4)	0.4277(3)	0.061(3)
C117	0.3931(8)	0.0428(6)	0.3914(3)	0.055(3)
O11	0.4625(6)	0.0091(5)	0.4053(3)	0.073(3)
C121	0.2260(5)	0.3630(4)	0.5801(2)	0.060(3)
C122	0.3126(5)	0.3331(4)	0.5866(2)	0.061(3)
C123	0.3374(5)	0.2807(4)	0.5556(3)	0.063(3)
C124	0.2757(6)	0.2584(3)	0.5180(3)	0.049(3)
C125	0.1891(5)	0.2883(4)	0.5115(2)	0.060(3)
C126	0.1642(4)	0.3406(4)	0.5425(3)	0.064(3)
C127	0.1988(7)	0.4188(4)	0.6132(3)	0.085(4)
O12A	0.256(2)	0.4486(18)	0.6406(10)	0.128(4)
Cl1A	0.0844(7)	0.4411(8)	0.6126(6)	0.118(3)1
O12B	0.1187(11)	0.4601(9)	0.6494(5)	0.128(4)
Fe2	0.39785(16)	0.58005(14)	0.29418(8)	0.0483(7)
C21	0.4970(7)	0.6415(6)	0.3265(3)	0.051(3)
C22	0.5317(6)	0.5957(6)	0.2931(4)	0.055(3)
C23	0.4838(7)	0.6113(6)	0.2484(3)	0.060(3)
C24	0.4194(7)	0.6669(6)	0.2541(3)	0.049(3)
C25	0.4276(7)	0.6855(5)	0.3024(3)	0.049(3)
C26	0.3436(9)	0.5220(7)	0.3418(3)	0.090(4)
C27	0.3765(8)	0.4751(6)	0.3084(4)	0.082(4)
C28	0.3299(9)	0.4923(7)	0.2637(3)	0.091(4)
C29	0.2681(8)	0.5498(7)	0.2694(4)	0.089(4)
C210	0.2766(8)	0.5682(6)	0.3177(5)	0.092(4)
C211	0.4794(6)	0.6946(4)	0.4096(3)	0.055(2)
C212	0.4470(6)	0.6714(3)	0.4505(3)	0.064(3)
C213	0.4211(6)	0.7223(5)	0.4821(2)	0.062(3)
C214	0.4275(5)	0.7964(4)	0.4729(3)	0.051(2)
C215	0.4598(6)	0.8196(3)	0.4320(3)	0.061(3)
C216	0.4858(6)	0.7687(5)	0.4004(2)	0.056(3)
C217	0.5160(8)	0.6404(6)	0.3778(3)	0.059(3)
O21	0.5590(6)	0.5868(5)	0.3964(3)	0.082(3)
C221	0.3415(5)	0.9483(4)	0.5717(2)	0.066(3)
C222	0.3638(6)	0.8768(4)	0.5845(2)	0.077(3)
C223	0.3915(6)	0.8286(3)	0.5518(3)	0.072(3)
C224	0.3970(5)	0.8520(4)	0.5062(3)	0.051(2)
C225	0.3747(6)	0.9235(4)	0.4934(2)	0.066(3)
C226	0.3469(6)	0.9716(3)	0.5262(2)	0.067(3)
C227	0.3129(4)	0.9992(4)	0.6074(3)	0.079(3)
O22	0.2918(7)	0.9830(6)	0.6477(3)	0.080(3)
Cl2	0.3083(4)	1.0914(3)	0.5909(2)	0.146(2)
Fe3	0.11857(16)	0.33022(14)	0.20654(9)	0.0507(8)
C31	0.1680(6)	0.2855(6)	0.1507(3)	0.048(3)
C32	0.1344(6)	0.2306(5)	0.1788(3)	0.053(3)
C33	0.1838(7)	0.2348(5)	0.2243(3)	0.054(3)
C34	0.2479(6)	0.2922(6)	0.2242(3)	0.053(3)
C35	0.2381(6)	0.3236(5)	0.1787(4)	0.047(3)
C36	0.0200(8)	0.4058(6)	0.1821(3)	0.073(4)
C37	−0.0173(7)	0.3479(6)	0.2063(4)	0.082(4)
C38	0.0273(8)	0.3467(6)	0.2529(4)	0.087(4)
C39	0.0922(8)	0.4039(7)	0.2575(3)	0.077(4)
C310	0.0877(8)	0.4405(6)	0.2137(4)	0.068(4)
C311	0.1502(6)	0.3556(4)	0.0743(2)	0.056(3)
C312	0.0874(4)	0.3984(5)	0.0468(3)	0.061(3)
C313	0.1168(5)	0.4491(4)	0.0160(3)	0.061(3)
C314	0.2089(6)	0.4569(4)	0.0127(2)	0.052(3)
C315	0.2716(4)	0.4140(4)	0.0403(3)	0.051(3)
C316	0.2423(5)	0.3634(4)	0.0711(3)	0.054(3)
C317	0.1170(7)	0.2986(6)	0.1047(3)	0.053(3)
O31	0.0486(7)	0.2609(5)	0.0906(3)	0.082(3)
C321	0.2884(5)	0.6165(4)	−0.0836(2)	0.056(3)
C322	0.2021(5)	0.5863(4)	−0.0914(2)	0.069(3)
C323	0.1760(5)	0.5334(4)	−0.0610(3)	0.064(3)
C324	0.2363(6)	0.5109(4)	−0.0230(3)	0.057(3)
C325	0.3226(5)	0.5411(4)	−0.0152(3)	0.062(3)
C326	0.3487(4)	0.5940(4)	−0.0456(3)	0.066(3)
C327	0.3178(6)	0.6726(4)	−0.1160(2)	0.077(3)
O32A	0.3925(9)	0.6944(10)	−0.1207(6)	0.082(4)
Cl3A	0.2316(5)	0.7136(5)	−0.1530(3)	0.093(3)
O32B	0.274(3)	0.7120(13)	−0.1438(8)	0.093(3)
Cl3B	0.4349(8)	0.6848(11)	−0.1144(7)	0.082(4)
Fe4	0.11508(18)	0.82839(13)	0.20849(9)	0.0500(7)
C41	0.0158(7)	0.8932(6)	0.1745(3)	0.046(3)
C42	−0.0214(7)	0.8413(5)	0.2034(4)	0.060(3)
C43	0.0182(7)	0.8530(6)	0.2503(3)	0.053(3)
C44	0.0799(7)	0.9122(6)	0.2503(3)	0.056(3)
C45	0.0784(7)	0.9371(5)	0.2035(4)	0.050(3)
C46	0.1806(8)	0.7760(7)	0.1588(3)	0.071(4)
C47	0.1349(7)	0.7246(6)	0.1845(4)	0.076(4)
C48	0.1701(7)	0.7310(6)	0.2325(4)	0.074(4)
C49	0.2374(7)	0.7863(6)	0.2365(3)	0.076(4)
C410	0.2440(6)	0.8142(6)	0.1910(4)	0.060(3)
C411	0.0298(6)	0.9407(4)	0.0925(3)	0.052(3)
C412	0.0626(6)	0.9160(3)	0.0521(3)	0.074(4)
C413	0.0893(6)	0.9658(5)	0.0200(3)	0.074(4)
C414	0.0832(6)	1.0402(5)	0.0283(3)	0.059(3)
C415	0.0504(6)	1.0649(3)	0.0687(3)	0.061(3)
C416	0.0237(6)	1.0151(5)	0.1008(3)	0.056(3)
C417	−0.0033(7)	0.8839(6)	0.1236(3)	0.051(3)
O41	−0.0497(5)	0.8318(5)	0.1060(3)	0.066(3)
C421	0.1661(6)	1.1973(4)	−0.0690(2)	0.073(3)
C422	0.1478(7)	1.1262(4)	−0.0842(2)	0.096(4)
C423	0.1212(7)	1.0744(3)	−0.0533(3)	0.095(4)
C424	0.1129(6)	1.0937(4)	−0.0073(3)	0.061(3)
C425	0.1312(6)	1.1647(5)	0.0079(2)	0.072(3)
C426	0.1578(6)	1.2166(4)	−0.0230(3)	0.079(4)
C427	0.1992(5)	1.2520(5)	−0.1006(3)	0.090(4)
O42A	0.2312(11)	1.2365(19)	−0.1364(5)	0.136(5)
Cl4A	0.1950(5)	1.3447(3)	−0.0889(3)	0.066(2)
O42B	0.2182(13)	1.3148(8)	−0.0911(9)	0.066(2)
Cl4B	0.2101(11)	1.2196(11)	−0.1556(4)	0.136(5)

Refined site-occupation factors

O12A and Cl1A	0.489(11)
O12B and Cl1B	0.511(13)

Table 2 (Continued)

Atom	x	y	z	U_{eq} [a]
O32A and Cl3A	0.697(11)			
O32B and Cl3B	0.303(11)			
O42A and Cl4A	0.563(11)			
O42B and Cl4B	0.437(11)			

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

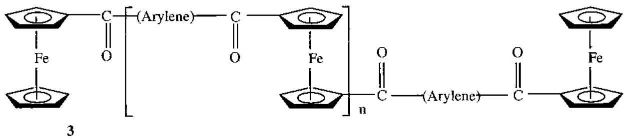
of the $COC_6H_4C_6H_4COCl$ groups confirmed the space group as *Cc*. Refinement, with the aryl and cyclopentadienyl rings modelled as planar regular pentagons and hexagons, respectively, was possible only in *Cc*. No solution or refinement was feasible in *C*2/*c*. At this point it was clear that the four independent iron atoms in *Cc* generated an almost exact $P2_1/c$ pattern of coordinates in the quartered cell. Because of the correlation introduced into the refinement by this pseudo-symmetry, the disorder of the CoCl groups in three of the four independent molecules, and the large number of parameters required for full anisotropic refinement, the subsequent refinement in *Cc* was carried out with the application of heavy restraints on the values of the displacement parameters. Refinement of the Flack parameter [12] gave a value of 0.56(5), implying racemic twinning [9].

Refined atom coordinates are in Table 2, and selected geometric parameters are in Table 3. Fig. 1 shows the four independent molecules in the structure, Fig. 2 shows the hydrogen-bonded dimer formed between molecules are types **1** and **3**, Fig. 3 shows one pair of molecules linked by aromatic π···π stacking, Fig. 4 shows one of the chains running parallel to the [1$\bar{1}$0] directions, and Fig. 5 shows a stereoview of the stacked [1$\bar{1}$0] and [110] chains.

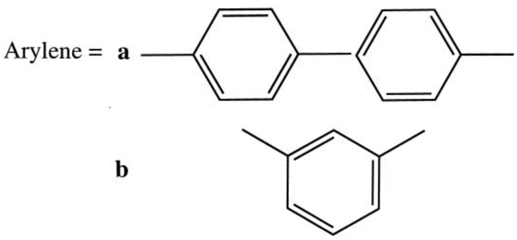
3. Results and discussion

3.1. Acylation reactions

Friedel–Crafts acylation of ferrocene using equimolar quantities of ferrocene and either 4,4′-bis(chlorocarbonyl)biphenyl or isophthaloyl dichloride lead, using extended reaction times in refluxing dichloromethane, to the precipitation of deep-red sparingly soluble materials, whose ^{1}H-NMR spectra were consistent with their formulation as ferrocene-terminated polyketone polymers of type **3**.



3



For **3a** and **3b** the NMR integration indicated mean values, $\bar{n}$, of ca. 3 and 24, respectively: it seems plausible that chain length is limited by the solubility of the growing polymer in the reaction medium, here of rather low polarity.

The principal purpose of the present study, however, has not been the characterisation of these polymeric products, but rather the characterisation of the early intermediates in polymer formation: by appropriate choice of reaction conditions it is possible to isolate and identity two early intermediates. When reactions with the same two acylating agents were carried out using a two-fold excess of ferrocene, so that no hetero-annular diacylation was required before the complete consumption of the acylating agent, the diketones **2a** and **2b** could be isolated in good yields. These products were identified by elemental analysis and by means of their particularly simple and characteristic ^{1}H- and ^{13}C-NMR spectra. The spectra for each of **2a** and **2b** contained the characteristic resonances of a mono-substituted ferrocene, the characteristic resonances of the symmetrically disubstituted arylene units 4,4′-$C_6H_4C_6H_4$ in **2a** and 1,3-C_6H_4 in **2b**, together with a single ketonic carbonyl resonance in the ^{13}C spectrum. Both crystallised with a very tiny crystal habit and, despite repeated efforts, no crystals suitable for single-crystal X-ray diffraction could be obtained.

When the reaction which gave compounds **2a** and **2b** were monitored by TLC, it was apparent that, in each case, formation of the diketone **2** was preceded by formation of another compound. TLC showed initial formation of an intermediate less polar than **2**, whose abundance grew to a maximum and then fell away as the abundance of **2** increased: the procedures used for the optimum production of compounds **2a** and **2b** involved reactions run until this less polar intermediate has wholly disappeared.

In order to isolate and identify these early intermediate, reactions of 1:1 stoichiometry designed to optimise their formation were conducted at 0°C with frequent monitoring by TLC: when the abundance of the early intermediate was judged to be at a maximum, each reaction was quenched and worked up in the usual manner. In this way, compounds **1a** and **1b** were isolated, albeit in very low yield in the case of **1b**. The constitution of **1a** was established by elemental analysis and NMR, and was confirmed by single-crystal X-ray structure analysis (see Section 3.2). The ^{13}C-NMR spectra of **1a** and **1b** both contained two resonances in the carbonyl region, one at ca. δ 198 characteristic of a ketone and a second at ca. δ 168; this is consistent with the presence of either a carboxylic acid or an acid chloride, and initially it was thought that the presence of a carboxyl group arising from hydrolysis during the work-up procedure was the more plausible. However the X-ray analysis of **1a** showed plainly that no hydrolysis had occurred. The near identity of the ^{13}C chemical shifts in **1a** and **1b**, particularly for the carbonyl groups, suggested that **1b** was also an acid chloride, rather than a carboxylic acid. This was confirmed by the lack of the characteristic carboxylic acid absorption in the IR spectra of **1a** and **1b**: in addition the ν(CO) values in **1a** and **1b** were within the range normally observed for aroyl chlorides, but significantly higher than those normally observed for aromatic carboxylic acids.

By contrast with the acylation behaviour of isophthaloyl dichloride to form **1b** and then **2b**, when the isomeric terephthaloyl dichloride was employed no diketone product was formed, even in prolonged reactions. The reaction conditions which led, in 8–10 h, to good yields of **2a** and **2b** gave only **1c**, even after 24 h. This product was again identified as an acid chloride by virtue of its carbonyl shift at δ 167.9, virtually identical with those in **1a** and **1b**, by the lack of carboxylic IR absorption, and by the high value of ν(CO). Plainly the subsequent reaction of **1c** as an acylating agent is extremely slow, while that of **1b** is the fastest of the three acid chlorides of type **1**, as judged by the very low maximal abundance of **1b** and the high isolated yield of **2b**.

With 1,3,5-benzenetricarbonyl trichloride, although the reaction with ferrocene is also slow, a 24 h reflux in CH_2Cl_2 permits the isolation of modest quantities of the triketone **4c**, again readily identified by its extremely simple ^{1}H- and ^{13}C-NMR spectra. These comprise the characteristic resonances for a single type of

Table 3
Selected torsional angles (°), hydrogen bonds (Å, °) and π···π interactions for **1a**

(a) *Torsional angles*

C122–C121–C127–O12A	14.0(8)	C113–C114–C124–C123	−25.6(7)
C122–C121–C127–Cl1A	−165.9(8)	C213–C214–C224–C223	20.6(7)
C122–C121–C127–O12B	−163.8(11)	C313–C314–C324–C323	−21.2(7)
C122–C121–C127–Cl1B	16.2(11)	C413–C414–C424–C423	19.1(8)
C222–C221–C227–O22	−12.2(5)	C112–C111–C117–O11	37.6(14)
C222–C221–C227–Cl2	167.9(4)	C212–C211–C217–O21	−35.8(14)
		C312–C311–C317–O31	39.3(14)
C322–C321–C327–O32A	−163.9(8)	C412–C411–C417–O41	−41.9(12)
C322–C321–C327–Cl3A	16.2(8)		
C322–C321–C327–O32B	19.9(10)	C12–C11–C117–O11	2.7(1)
C322–C321–C327–Cl3B	−160.1(10)	C22–C21–C217–O21	−10.5(17)
		C32–C31–C317–O31	−2.4(15)
C422–C421–C427–O42A	−16.9(6)	C42–C41–C417–O41	0.8(14)
C422–C421–C427–Cl4A	−163.2(5)		
C422–C421–C427–O42B	−179.1(9)		
C422–C421–C427–Cl4B	0.9(9)		

(b) *Hydrogen bonds*

	D–H	H···A	D···A	D–H···A
C123–H123···O31 [a]	0.93	2.37	3.265(13)	161
C223–H223···O41 [b]	0.93	2.49	3.391(11)	164
C323–H323···O11 [c]	0.93	2.39	3.294(12)	164
C423–H423···O21 [d]	0.93	2.45	3.368(11)	168

(c) π···π *Interactions*

Ring 1	Ring 2	Dihedral angle (°)	Perp. distance (Å)	Offset (Å)
C12*n*	C32*n* [e]	1.1	3.52	1.32
C22*n*	C42*n* [f]	1.8	3.72	1.26

[a] Symmetry codes: $0.5+x$, $0.5-y$, $0.5+z$.

[b] $0.5+x$, $1.5-y$, $0.5+z$.

[c] $-0.5+x$, $0.5-y$, $-0.5+z$.

[d] $-0.5+x$, $1.5-y$, $-0.5+z$.

[e] x, $1-y$, $0.5+z$.

[f] x, $2-y$, $0.5+z$.

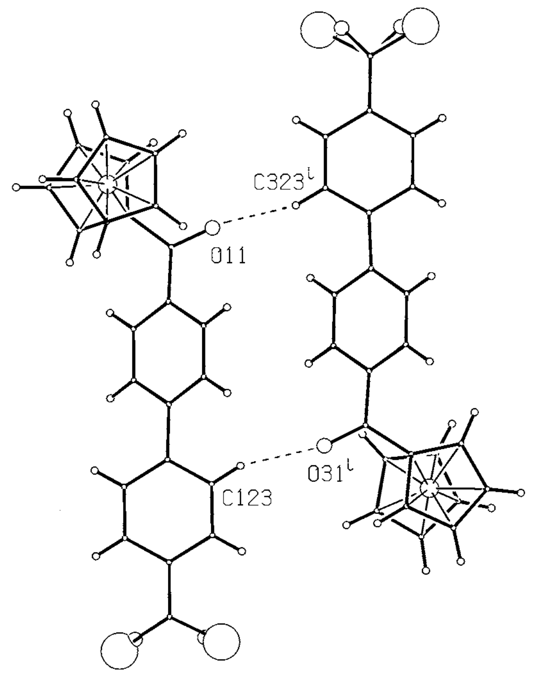


Fig. 2. The cyclic dimer formed by molecules of types 1 and 3, showing the $R^2_2(18)$ ring formed by the two C–H···O hydrogen bonds.

mono-substituted ferrocene together with a single aromatic resonance in the ^{1}H spectrum and, in the ^{13}C spectrum, two aromatic resonances, one C–H and one quaternary, and a ketonic carbonyl resonance.

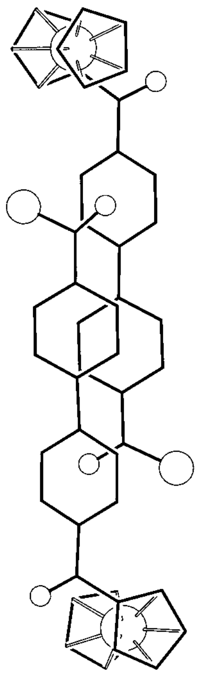


Fig. 3. View of one pair of π-stacked molecules, formed by molecules of types 1 and 3, showing the ring offset approximately equal to the radius of an aryl ring. For the sake of clarity, only the major conformation of the chlorocarbonyl groups is shown, and H atoms are omitted.

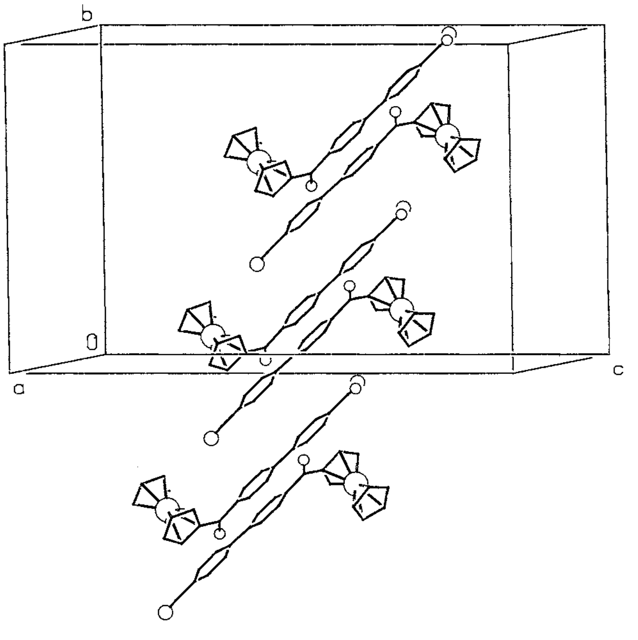
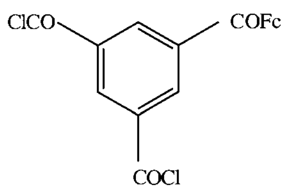
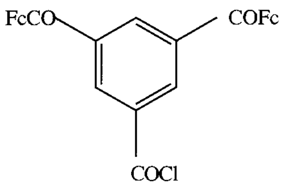


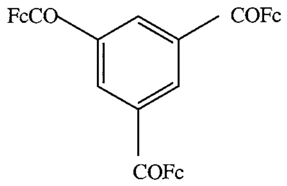
Fig. 4. View of one of the [1$\bar{1}$0] chains built from molecules of types 1 and 3: atoms are depicted as in Fig. 3.



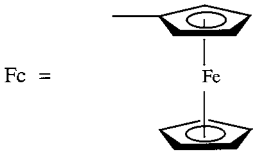
4a



4b



4c



Aside from the characteristic resonances of a mono-substituted ferrocene, the ^{1}H spectrum of **4c** contains only a single sharp absorption, while the ^{13}C spectrum contains just three other resonances, two arising from the aryl ring and one from the ketonic carbonyl group. Monitoring of this acylation by TLC showed that, as expected, there were two intermediates formed before **4c** and these are plausibly identified as the mono- and bi-ferrocenyl species **4a** and **4b**, respectively, although no attempt was made to isolate these.

3.2. Crystal and molecular structure of ***1a***

The asymmetric unit of compound **1a** consists of four independent molecules (Fig. 1), and it was clear from an early stage in the refinement that this compound is indeed an acyl chloride rather than a carboxylic acid, as demonstrated by the bond distances and the behaviour of the displacement parameters. In three of these molecules, those containing Fe1, Fe3 and Fe4, the terminal chlorocarbonyl groups is disordered with two orientations of this fragment differing by a 180° rotation about the exocyclic C(aryl)–C(O)Cl bond (Fig. 1). For the three molecules disordered in this manner, the two orientations are in the ratios 0.51(1):0.49(1), 0.70(1):0.30(1) and 0.56(1):0.44(1), respectively. Further evidence that there are no COO groups in **1a** is provided by the absence of the characteristic association into $R^2_2(8)$dimers [13].

As is often observed in systems where there is an excess of hard [14] hydrogen-bond acceptors, in this case the ketonic oxygen atoms, there are C–H···O hydrogen bonds with aryl carbon atoms acting as the donors. The pairwise development of such interactions serves to link pairs of molecules into cyclic dimers (Table 3). The C–H group C123–H in molecule 1 at (x, y, z) acts as a donor towards the ketonic oxygen O31 in molecule 3 at ($0.5+x$, $0.5-y$, $0.5+z$), while C323–H in molecule 3 at ($0.5+x$, $0.5-y$, $0.5+z$) in turn acts as donor to O11 in molecule 1 at (x, y, z), so generating a dimeric motif (Fig. 2) characterised by an $R^2_2(18)$ring [13]. Similarly molecule 2 at (x, y, z) and molecule 4 at ($0.5+x$, $1.5-y$, $0.5+z$) are linked by a pair of C–H···O hydrogen bonds into a second $R^2_2(18)$motif. These four independent C–H···O hydrogen bonds (Table 3) all have d(H···O) (un-normalised) < 2.50 Å, d(C···O) $<$ 3.40 Å, and angle(C–H···O) $> 160°$. Hence all should be regarded as strong examples of their type [15]. The strength of these hydrogen bonds depends upon the fact that aromatic carbon atoms are amongst the best donors in C–H···A (A, acceptor) hydrogen bonds, while ketonic carbonyl groups are second only to sulfoxide and sulfone S=O groups as neutral hydrogen-bond acceptors. The two independent $R^2_2(18)$rings are both approximately centrosymmetric around the points (0.5, 0.125, 0.5) and (0.5, 0.625, 0.5), respectively: in the $P2_1/c$ solution, these rings would be precisely centrosymmetric.

These dimers are themselves linked into chains by means of π···π stacking interactions [16] in which aryl rings of molecules in neighbouring dimer units are essentially parallel with perpendicular separations of 3.5–3.7 Å and with their ring centroids offset by approximately the radius of an aryl ring (Fig. 3 and Table 3), the ideal for such interactions [16]. The ring C12n ($n = 1$–6) in molecule 1 within the dimer centred near (0.5, 0.125, 0.5) interacts in this manner with ring C32n in molecule 3 within the dimer around (0, 0.625, 0.5), while molecule 3 within the (0.5, 0.125, 0.5) dimer interacts similarly with molecule 1 in the dimer around (1, −0.375, 0.5). These interactions generate a chain parallel to $[1\bar{1}0]$ and passing through the point (0.5, 0, 0.5) (Fig. 4). The dimers formed by molecules of types 2 and 4 form a similar chain, parallel to the first but passing through the point (0.5, 0.5, 0.5). Each of these chains is in fact generated by the action of the C-centring operation in the space group Cc.

This array of parallel chains utilises only half the contents of the unit cell, and lies largely in the domain $0.2 < z < 0.75$. A similar array lying in the domain $0.7 < z < 1.25$ is generated from the first by the action of the glide planes and runs parallel to the [110] direction. The entire structure is built up from a stack of these arrays, having alternating directions in a criss-cross mesh, where the angle between the directions of the crossing chains is ca. 78° (Fig. 5).

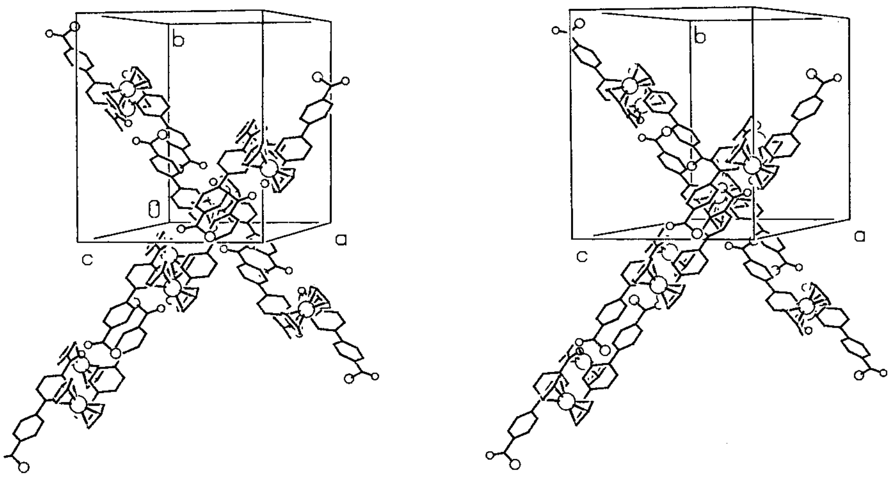


Fig. 5. Stereoview of the stacked $[1\bar{1}0]$ and [110] chains.

4. Conclusions

The acylation of ferrocene using arylene bis-acid chlorides proceeds via the keto-acid chlorides **1** and the diketones **2**. However, at no stage was any evidence found for hetero-annular bis-diacylation of a single ferrocene nucleus to provide products of type $Fe[C_5H_4CO(arylene)COCl]_2$. Hence acylation of an unsubstituted ferrocene nucleus by the species **1a** and **1b**, to give **2a** and **2b**, respectively, is significantly faster than the further acylation of the intermediates of type **1** by the initial bis-acid chlorides: on the other hand, the acylation reactions of **1c** appear to be exceedingly slow, so that no diketone **2c** was obtained. Hence hetero-annular bis-diacylation occurs for **2a** and **2b**, but not for **1a** or **1b**.

The isolation of the primary reaction products as the acid chlorides **1** rather than as the corresponding carboxylic acids implies very slow hydrolysis in the aqueous work-up and subsequent chromatography. In general, acyl halides undergo rapid hydrolysis only if they are appreciably soluble in water. Aromatic acyl halides are poorly soluble in water and hence undergo much slower hydrolysis [17]: thus even benzoyl chloride is scarcely soluble in water, so allowing benzoylations of, for example, alcohols and amines to be conducted efficiently in alkaline aqueous solution. The acid chlorides **1** are expected to be even less soluble in water than benzoyl chloride, so leading to extremely slow hydrolysis.

The crystal structure of compound **1a** was originally undertaken to provide proof of constitution: despite the aqueous work-up followed by chromatography on silica, compounds **1a**–**1c** were all deduced from spectral and analytical data to be acid chlorides rather than carboxylic acids. The single-crystal X-ray diffraction study certainly provided unambiguous proof of the acid chloride constitution and, in addition, revealed extensive intramolecular association involving both strong C–H···O hydrogen bonds and aromatic π···π interactions. Thus a study originally intended simply as a structure proof turned out to reveal highly interesting supramolecular interactions.

5. Supplementary material

Additional data, comprising full details of the molecular geometries and the displacement parameters, have been deposited at the Cambridge Crystallographic Data Centre, CSD-116264 for compound **1a**.

Acknowledgements

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